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### (54) **Plating method and plating apparatus**

(57) The present invention relates to a plating method and a plating apparatus which can attain embedding of copper into fine interconnection patterns with the use of a plating liquid having high throwing power and leveling properties, and which can make the film thickness of the plated film substantially equal between the interconnection region and the non-interconnection region, thereby facilitating a later CMP processing. A plating

method comprising filling a plating liquid containing metal ions and an additive into a plating space formed between a substrate and an anode disposed closely to the substrate so as to face the substrate, and changing the concentration of the additive in the plating liquid filled into the plating space during a plating process.

EP 1 191 128 A2

## Description

## BACKGROUND OF THE INVENTION

## Field of the Invention:

[0001] The present invention relates to a plating method and a plating apparatus, and more particularly to a plating method and a plating apparatus for filling a metal such as copper (Cu) or the like into fine interconnection patterns (trenches) on a semiconductor substrate.

## Description of the Related Art:

[0002] Aluminum or aluminum alloy has generally been used as a material for forming interconnect circuits on semiconductor substrates. As the integrated density increases in recent years, there is a demand for the usage of a material having a higher conductivity as an interconnect material. It has been proposed to plate a substrate having interconnect pattern trenches thereon to fill the trenches with copper or its alloy.

[0003] There are known various processes including CVD (chemical vapor deposition), sputtering, etc. to fill interconnect pattern trenches with copper or its alloy. However, the CVD process is costly for forming copper interconnections, and the sputtering process fails to embed copper or its alloy in interconnect pattern trenches when the interconnect pattern trenches have a high aspect ratio, i.e., a high ratio of depth to width. The plating process is most effective to deposit a metal layer of copper or its alloy on a substrate to form copper interconnections thereon.

[0004] Various processes are available for plating semiconductor substrates with copper. They include a process of immersing a substrate in a plating liquid held at all times in a plating tank, referred to as a cup-type or dipping-type process, a process of holding a plating liquid in a plating tank only when a substrate, to be plated, is supplied to the plating tank, an electric plating process for plating a substrate with a potential difference, and an electroless plating process for plating a substrate with no potential difference.

[0005] In carrying out filling the fine interconnect patterns with copper by an electric copper-plating using a copper sulfate solution as a plating liquid, it is required to perform the plating process with high throwing power and high leveling properties. With a view to meeting this requirement, it is generally conducted to add to the plating liquid a compound called additive.

[0006] Such additives, generally in use, include:

sulfur compounds called "carrier" which grow crystal nuclei all over the plated surface, thereby promoting deposition of finer particles;

polymers which increase the overvoltage of copper deposition, thereby enhancing throwing power; and nitrogen compounds called "leveler" which adhere to convex portions, where the plating preferentially grows, to thereby increase the overvoltage and retard the copper deposition at the convex portions, thereby providing a flat plated layer.

[0007] However, when the filling the fine interconnect patterns with copper by an electric copper-plating is conducted by using a plating liquid which, due to the use of the above additives, has enhanced throwing power and leveling properties, there occurs a phenomena that the film thickness of the interconnection region of a substrate becomes thicker than the film thickness of the non-interconnection region. The unevenness in film thickness is not a problem in filling the interconnection region with copper; however, the unevenness makes it difficult to obtain a flat surface by a later CMP (chemical mechanical polishing) processing.

[0008] The plating treatment of a substrate for filling the interconnect pattern trenches with a metal, such as copper or its alloy, may be carried out by using a plating apparatus as shown in FIG. 30. As shown in FIG. 30, a substrate W and an anode 302 are disposed in parallel, facing each other, in a plating tank 301 accommodating a plating liquid 300. Plating is conducted by flowing a plating current i between the substrate W and the anode 302. The film thickness h of the plated film formed at a certain point on the surface of the substrate W is proportional to the product of the plating current value i and the energization time. The plating current value i in FIG. 30 is defined by the following formula (1):

$$i = E / (R1 + R2 + R3 + R4) \quad (1)$$

[0009] In the above formula (1), E represents power source voltage, R1 the anodic polarization resistance, R2 the resistance of the plating liquid 300, R3 the substrate (cathodic) polarization resistance, and R4 the sheet resistance

of the substrate W at the certain point. The anodic polarization resistance R1 and the substrate polarization resistance R3 are the interfacial resistances of the anode 302 and of the substrate W, respectively, and change with the concentration of the additive or of the plating liquid. The resistance R2 of the plating liquid 300 is proportional to the distance between the anode 302 and the substrate (cathode) W.

[0010] The electric supply to the substrate W is made via a cathode electrode 303 which is generally connected to the peripheral end of the substrate W. Accordingly, the sheet resistance R4 at a point increases as the distance from the peripheral end of the substrate W increases, i.e., as the point comes near to the center P of the substrate W. Therefore, the plating current value  $i$  on the inner central side of the substrate W is smaller than that on the outer peripheral side (see the above formula (1)), whereby it is likely that the film thickness becomes smaller on the inner central side compared to the outer peripheral side. There has thus been the problem in conventional plating apparatuses that a plated film having a uniform film thickness over the entire substrate surface is hard to form. Especially when an LSI interconnection is formed by plating, the small thickness, generally 50-200 nm, of the seed layer of the substrate (Si substrate) makes the sheet resistance R4 considerably larger. Such a large sheet resistance R4 has a larger influence on the film thickness.

## SUMMARY OF THE INVENTION

[0011] The present invention has been made in view of the above drawbacks in the related art. It is therefore a first object of the present invention to provide a plating method and a plating apparatus which can attain embedding of copper into fine interconnect patterns with the use of a plating liquid having high throwing power and leveling properties, and which can make the film thickness of the plated film substantially equal between the interconnection region and the non-interconnection region, thereby facilitating a later CMP processing.

[0012] It is a second object of the present invention to provide a plating apparatus and a plating method which can form a plated film having a more uniform film thickness over the entire surface of a substrate.

[0013] In order to achieve the first object, the present invention provides a plating method, comprising: filling a plating liquid containing metal ions and an additive into a plating space formed between a substrate and an anode disposed closely to the substrate so as to face the substrate; and changing the concentration of the additive in the plating liquid filled into the plating space during a plating process.

[0014] In the course of plating of a substrate, the concentration of an additive in a plating liquid filled into the plating space formed between a substrate and an anode gradually decreases with the process of plating due to the take-in of the additive within the deposited metal film and the oxidation degradation at the anode. The change of additive concentration is larger in cases where ① the plating of a substrate is by a close-to-anode plating where the amount of the plating liquid itself is small, ② the introduction of a plating liquid into the plating space is conducted only before plating, and not conducted during plating (batch-wise introduction), and ③ a plating liquid is introduced intermittently during plating. The concentration change of the plating liquid is larger when, during a plating process, an additional solution or a plating liquid containing a different concentration of additive is separately introduced into the plating space with a separate liquid introduction device.

[0015] By thus changing the additive concentration of the plating liquid filled into the plating space during the plating process, the unevenness in the plated film thickness between the interconnection region and the non-interconnection region is reduced or corrected.

[0016] It is not fully clarified by what mechanism the difference in film thickness between the interconnection and non-interconnection regions is corrected by making a change in the additive concentration, during the plating process, of the plating liquid filled into the plating space. Anyway, in general, the difference in film thickness can be effectively corrected when the concentration of an additive decreases during the plating process, when the concentration of a particular additive, especially a plating-promoting additive called "brightener", is set at a high value, or when the content of an additive is significantly lowered by, for example, adsorption removal of the additive. The film-thickness difference in question is considered to be produced at the middle or later stage of the plating process when the metal filling into the fine interconnect trenches has almost been completed. Accordingly, making the change in additive concentration of the plating liquid at the middle or later stage of plating is more effective than that at the initial stage when the metal filling into interconnect trenches is in progress.

[0017] The concentration of an additive in the plating liquid can be adjusted by intermittently supplying the plating liquid into the plating space.

[0018] The additive concentration can also be adjusted by supplementary addition of the additive to the plating space, or by removal of the additive in the plating liquid.

[0019] The present invention also provides a plating apparatus, comprising: a substrate holder for holding a substrate so that a current can flow from a cathode to the substrate; an anode opposed to the substrate held by the substrate holder; and a plating liquid introducing device for introducing a plating liquid into a plating space formed between the substrate and the anode in a *batch* process or an intermittent process.

**[0020]** This apparatus can perform a plating treatment while changing the concentration of an additive in the plating liquid filled into the plating space.

**[0021]** A plating liquid impregnation material may be provided in the plating space. The plating liquid impregnation material, e.g. synthetic fibers can adsorb and remove a particular additive component, e.g. a leveler, and thus is effective for reducing the leveler concentration of the plating liquid.

**[0022]** Further, the plating apparatus may be provided with a liquid introducing device for introducing into the plating space a liquid having a different additive concentration from that in the above plating liquid. The addition of the liquid (solution or plating liquid) having the different additive concentration makes it possible to arbitrarily control, during the plating process, the change of additive concentration in the plating liquid filled into the plating space formed between the substrate and the anode. For example, the addition of the liquid having a higher leveler concentration, during the plating process, can correct the film-thickness difference.

**[0023]** The plating apparatus may also be provided with a temperature adjusting device for adjusting the temperature of the plating liquid in the plating space. Since the adsorption reaction which occurs on the above plating liquid impregnation material is highly temperature-dependent, the use of a higher plating liquid temperature generally increases the adsorption capacity of the plating liquid impregnation material.

**[0024]** In order to achieve the second object, the present invention provides a plating apparatus, comprising: a substrate holder for holding a substrate so that a current can flow from a cathode to the substrate; an anode opposed to the substrate held by the substrate holder; and a moving device for moving a portion of the substrate facing the anode in such a state that an inner central portion of the surface of the substrate faces the anode for a longer time than an outer peripheral portion of the surface of the substrate faces the anode.

**[0025]** This plating apparatus can make the energization time of a plating current to the inner central portion of a substrate longer than the energization time of the plating current to the outer peripheral portion, thereby making the products of the electric current values and the energization times of the electric current at various points of the substrate equal over the entire surface of the substrate. This enables the formation of a plated film having a uniform film thickness over the entire surface of a substrate.

**[0026]** The moving device may comprise a substrate-rotating device for rotating a substrate, an anode-rotating device for rotating an anode, or an anode-translating device for translating an anode.

**[0027]** The present invention also provides another plating apparatus comprising: a substrate holder for holding a substrate so that a current can flow from a cathode to the substrate; and an anode opposed to the substrate held by the substrate holder, wherein the distance between the anode and an inner central portion of the substrate is smaller than the distance between the anode and an outer peripheral portion of the substrate.

**[0028]** This apparatus can make the resistance of a plating liquid at the inner central portion of the substrate smaller than that at the outer peripheral portion of the substrate, thereby making the electric current value more equal at the inner central portion of the substrate to at the outer peripheral portion of the substrate, whereby the film thickness of the plated film formed on the substrate can be made uniform over the entire surface of the substrate.

**[0029]** The present invention further provides a yet another plating apparatus comprising: a substrate holder for holding a substrate so that a current can flow from a cathode to the substrate; an anode opposed to the substrate held by the substrate holder; and a distance changing device for changing the distance between the substrate and the anode after initiation of plating.

**[0030]** At the initiation of plating, the potential gradient on the inner central side of the substrate is higher than the potential gradient on the outer peripheral side, whereby a larger amount of plated film is formed on the inner side of the substrate. This situation can be reversed according to this apparatus, by later making the distance between the substrate and the anode larger. As a result, a plated film having a uniform film thickness over the entire surface of the substrate can be obtained.

**[0031]** The present invention also provides a plating method, comprising: disposing a substrate and an anode in such a state that the substrate faces the anode; flowing a current between the substrate and the anode while supplying a plating liquid therebetween; and moving a portion of the substrate facing the anode in such a state that an inner central portion of the surface of the substrate faces the anode for a longer time than an outer peripheral portion of the surface of the substrate faces the anode.

**[0032]** The present invention also provides another plating method, comprising: disposing a substrate and an anode in a state that the substrate faces the substrate; and flowing a current between the substrate and the anode while supplying a plating liquid therebetween, wherein the distance between the anode and an inner central portion of the substrate is smaller than the distance between the anode and an outer peripheral portion of the substrate.

**[0033]** The present invention further provides yet another plating method, comprising: disposing a substrate and an anode in a state that the substrate faces the anode; flowing a current between the substrate and the anode while supplying a plating liquid therebetween; and changing the distance between the substrate and the anode after initiation of plating.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0034]

5 FIGS. 1A to 1C are sectional views showing an example of a process for performing plating by a plating apparatus and a plating method of the present invention;  
 FIG. 2 is a plan view showing the whole of the plating apparatus according to a first embodiment of the present invention;  
 FIG. 3 is a plan view showing a plating unit;  
 10 FIG. 4 is a sectional view taken on line A-A of FIG. 3;  
 FIG. 5 is an enlarged sectional view of a substrate holder and a cathode portion;  
 FIG. 6 is a front view of FIG. 3;  
 FIG. 7 is a right side view of FIG. 3;  
 FIG. 8 is a rear view of FIG. 3;  
 15 FIG. 9 is a left side view of FIG. 3;  
 FIG. 10 is a front view showing a pre-coating/recovering arm;  
 FIG. 11 is a plan view of the substrate holder;  
 FIG. 12 is a sectional view taken on line B-B of FIG. 11;  
 FIG. 13 is a sectional view taken on line C-C of FIG. 11;  
 20 FIG. 14 is a plan view of the cathode portion;  
 FIG. 15 is a sectional view taken on line D-D of FIG. 14;  
 FIG. 16 is a plan view of an electrode arm;  
 FIG. 17 is a longitudinal sectional front view of FIG. 16;  
 FIG. 18 is a sectional view taken on line E-E of FIG. 16;  
 25 FIG. 19 is an enlarged view showing a part of FIG. 18 in an enlarged manner;  
 FIG. 20 is a plan view of a state in which a housing of an electrode portion of the electrode arm has been removed;  
 FIG. 21 is a longitudinal sectional front view of an electrode arm containing a substrate holder according to a second embodiment of the present invention;  
 FIG. 22 is a plan view showing the relationship between a substrate and an anode according to the second embodiment of the present invention;  
 30 FIG. 23 is a plane view of an electrode arm according to a third embodiment of the present invention;  
 FIG. 24 is a plan view showing the relationship between a substrate and an anode according to the third embodiment of the present invention;  
 FIG. 25 is a pattern diagram showing the relationship between a substrate and an electrode portion according to a fourth embodiment of the present invention;  
 35 FIG. 26 is a pattern diagram showing the relationship between a substrate and an electrode portion according to a fifth embodiment of the present invention;  
 FIG. 27A is a pattern diagram showing the relationship between a substrate and an anode at the initiation of plating according to a sixth embodiment of the present invention;  
 40 FIG. 27B is a pattern diagram showing the relationship between the substrate and the anode at the completion of plating according to the sixth embodiment of the present invention;  
 FIG. 28A is a isoelectric line diagram showing the state of electric field between the anode and the substrate in the relationship of FIG. 27A;  
 FIG. 28B is a isoelectric line diagram showing the state of electric field between the anode and the substrate in the relationship of FIG. 27B;  
 45 FIG. 29 is a sectional view of a face-down type plating apparatus according to a seventh embodiment of the present invention; and  
 FIG. 30 is a view showing a circuit typically formed by a conventional plating apparatus and its plating treatment.

## 50 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0035] An embodiment of the present invention will be described below with reference to the drawings. A substrate plating apparatus according to this embodiment is used to apply copper electroplating onto the surface of a semiconductor substrate, thereby obtaining a semiconductor apparatus having interconnects comprising a copper layer formed thereon. This plating process will be explained with reference to FIGS. 1A through 1C.

55 [0036] As shown in FIG. 1A, an oxide film 2 of  $\text{SiO}_2$  is deposited on the conductive layer 1a on a semiconductor substrate 1 on which semiconductor devices are formed. A contact hole 3 and a trench 4 for an interconnect are formed by lithography and etching technology. A barrier layer 5 of TiN or the like is formed thereon, and then a seed layer 7

as an electric supply layer for electroplating is formed on the barrier layer 5.

**[0037]** Then, as shown in FIG. 1B, the surface of the semiconductor substrate W is coated with copper by copper electroplating to deposit a plated copper film 6 on the oxide film 2, thus filling the contact hole 3 and the trench 4 of the semiconductor substrate 1 with copper. Thereafter, the plated copper film 6 on the oxide film 2 are removed by chemical mechanical polishing (CMP), thus making the plated copper film 6 in the contact hole 3 and the trench 4 lie flush with the oxide film 2. In this manner, an interconnect composed of the plated copper film 6 is formed as shown in FIG. 1C.

**[0038]** FIG. 2 is a plan view showing the whole of a plating apparatus for a substrate according to an embodiment of the present invention. As shown in FIG. 2, this plating apparatus has a rectangular facility which houses therein two loading/unloading units 10 for housing a plurality of substrates W therein, two plating units 12 for performing plating treatment and treatment incidental thereto, a transfer robot 14 for transferring substrates W between the loading/unloading units 10 and the plating units 14, and plating liquid supply equipment 18 having a plating liquid tank 16.

**[0039]** The plating liquid used in this embodiment contains the following additives: a sulfur-containing compound, such as thiourea and acrylic thiourea, as a carrier (brightener); polyether, polyethylene glycol or their derivatives as a polymer; and a nitrogen compound having a positive charge, such as polyamine or dyestuffs, as a leveler. Of course, the present invention is not limited to the use of these additives.

**[0040]** The plated unit 12, as shown in FIG. 3, is provided with a substrate treatment section 20 for performing plating treatment and treatment incidental thereto, and a plating liquid tray 22 for storing a plating liquid is disposed adjacent to the substrate treatment section 20. There is also provided an electrode arm 30 having an electrode portion 28 which is held at the front end of an arm 26 swingable about a rotating shaft 24 and which is swung between the substrate treatment section 20 and the plating liquid tray 22. Furthermore, a pre-coating/recovering arm 32, and fixed nozzles 34 for ejecting pure water or a chemical liquid such as ion water, and further a gas or the like toward a substrate are disposed laterally of the substrate treatment section 20. In this embodiment, three of the fixed nozzles 34 are disposed, and one of them is used for supplying pure water.

**[0041]** The substrate treatment section 20, as shown in FIGS. 4 and 5, has a substrate holder 36 for holding a substrate W with its surface to be plated facing upward, and a cathode portion 38 located above the substrate holder 36 so as to surround a peripheral portion of the substrate holder 36. Further, a substantially cylindrical bottomed cup 40 surrounding the periphery of the substrate holder 36 for preventing scatter of various chemical liquids used during treatment is provided so as to be vertically movable by an air cylinder 42.

**[0042]** The substrate holder 36 is adapted to be raised and lowered by the air cylinder 44 between a lower substrate transfer position A, an upper plating position B, and a pre-treatment/cleaning position C intermediate between these positions, as shown in FIG. 5. The substrate holder 36 is also adapted to rotate at an arbitrary acceleration and an arbitrary velocity integrally with the cathode portion 38 by a rotating motor 46 and a belt 48 (see FIG. 4). A substrate carry-in and carry-out opening 50 is provided in confrontation with the substrate transfer position A in a frame side surface of the plating unit 12 facing the transfer robot 14, as shown FIG. 7. When the substrate holder 36 is raised to the plating position B, a seal member 90 and cathode electrodes 88 (to be described below) of the cathode portion 38 are brought into contact with the peripheral edge portion of the substrate W held by the substrate holder 36. On the other hand, the cup 40 has an upper end located below the substrate carry-in and carry-out opening 50, and when the cup 40 ascends, the upper end of the cup 40 reaches a position above the cathode portion 38 closing the substrate carry-in and carry-out opening 50, as shown by imaginary lines in FIG. 5.

**[0043]** The plating liquid tray 22 serves to wet a plating liquid impregnation material 110 and an anode 98 (to be described later on) of the electrode arm 30 with a plating liquid, when plating has not been performed. As shown in FIG. 6, the plating liquid tray 22 is set at a size in which the plating liquid impregnation material 110 can be accommodated, and the plating liquid tray 22 has a plating liquid supply port and a plating liquid drainage port (not shown). A photo-sensor is attached to the plating liquid tray 22, and can detect brimming with the plating liquid in the plating liquid tray 22, i.e., overflow, and drainage. A bottom plate 52 of the plating liquid tray 22 is detachable, and a local exhaust port (not shown) is installed around the plating liquid tray.

**[0044]** As shown in FIGS. 8 and 9, the electrode arm 30 is vertically movable by a motor 54 and a ball screw, not shown, and swingable between the plating liquid tray 22 and the substrate treatment section 20 by a motor 56.

**[0045]** As shown in FIG. 10, the pre-coating/recovering arm 32 is coupled to an upper end of a vertical support shaft 58. The pre-coating/recovering arm 32 is swingable by a rotary actuator 60 and is also vertically moveable by an air cylinder 62 (see FIG. 7). The pre-coating/recovering arm 32 supports a pre-coating nozzle 64 for discharging a pre-coating liquid, on its free end, and a plating liquid recovering nozzle 66 for recovering the plating liquid, on a portion closer to its proximal end. The pre-coating nozzle 64 is connected to a syringe that is actuable by an air cylinder, for example, for intermittently discharging a pre-coating liquid from the pre-coating nozzle 64. The plating liquid recovering nozzle 66 is connected to a cylinder pump or an aspirator, for example, to draw the plating liquid on the substrate from the plating liquid recovering nozzle 66.

**[0046]** As shown in FIGS. 11 through 13, the substrate holder 36 has a disk-shaped substrate stage 68 and six

vertical support arms 70 disposed at spaced intervals on the circumferential edge of the substrate stage 68 for holding a substrate W in a horizontal plane on respective upper surfaces of the support arms 70. A positioning plate 72 is mounted on an upper end one of the support arms 70 for positioning the substrate by contacting the end face of the substrate. A pressing finger 74 is rotatably mounted on an upper end of the support arm 70 which is positioned opposite to the support arm 70 having the positioning plate 72 for abutting against an end face of the substrate W and pressing the substrate W the positioning plate 72 side when rotated. Chucking fingers 76 are rotatably mounted on upper ends of the remaining four support arms 70c for pressing the substrate W downwardly and gripping the circumferential edge of the substrate W.

[0047] The pressing finger 74 and the chucking fingers 76 have respective lower ends coupled to upper ends of pressing pins 80 that are normally urged to move downwardly by coil springs 78. When the pressing pins 80 are moved downwardly, the pressing finger 74 and the chucking fingers 76 are rotated radially inwardly into a closed position. A support plate 82 is disposed below the substrate stage 68 for engaging lower ends of the opening pins 80 and pushing them upwardly.

[0048] When the substrate holder 36 is located in the substrate transfer position A shown in FIG. 5, the pressing pins 80 are engaged and pushed upwardly by the support plate 82, so that the pressing finger 74 and the chucking fingers 76 rotate outwardly and open. When the substrate stage 68 is elevated, the opening pins 80 are lowered under the resiliency of the coil springs 78, so that the pressing finger 74 and the chucking fingers 76 rotate inwardly and close.

[0049] As shown in FIGS. 14 and 15, the cathode portion 38 comprises an annular frame 86 fixed to upper ends of vertical support columns 84 mounted on the peripheral edge of the support plate 82 (see FIGS. 5 and 13), a plurality of, six in this embodiment, cathode electrodes 88 attached to a lower surface of the annular frame 86 and projecting inwardly, and an annular sealing member 90 mounted on an upper surface of the annular frame 86 in covering relation to upper surfaces of the cathode electrodes 88. The sealing member 90 is adapted to have an inner peripheral edge portion inclined inwardly downwardly and progressively thin-walled, and to have an inner peripheral end suspending downwardly.

[0050] When the substrate holder 36 has ascended to the plating position B, as shown FIG. 5, the cathode electrodes 88 are pressed against the peripheral edge portion of the substrate W held by the substrate holder 36 for thereby causing electric current to flow through the substrate W. At the same time, an inner peripheral end portion of the seal member 90 is brought into contact with an upper surface of the peripheral edge of the substrate W under pressure to seal its contact portion in a watertight manner. As a result, the plating liquid supplied onto the upper surface (surface to be plated) of the substrate W is prevented from seeping from the end portion of the substrate W, and the plating liquid is prevented from contaminating the cathode electrodes 88.

[0051] In the present embodiment, the cathode portion 38 is vertically immovable, but rotatable integrated with the substrate holder 36. However, the cathode portion 38 may be arranged such that it is vertically movable and the sealing member 90 is pressed against the surface, to be plated, of the substrate W when the cathode portion 38 is lowered.

[0052] As shown in FIGS. 16 through 20, the electrode head 28 of the electrode arm 30 comprises a housing 94 coupled to a free end of the swing arm 26 through a ball bearing 92, a cylindrical support frame 96 surrounding the housing 94, and an anode 98 fixed by having a peripheral edge portion gripped between the housing 94 and the support frame 96. The anode 98 covers an opening of the housing 94, which has a suction chamber 100 defined therein. In the suction chamber 100, there is disposed a diametrically extending plating liquid introduction pipe 104 connected to a plating liquid supply pipe 102 which extends from the plating liquid supply unit 18 (see FIG. 2), and held in abutment against an upper surface of the anode 98. A plating liquid discharge pipe 106 communicating with the suction chamber 100 is connected to the housing 94.

[0053] The plating liquid introduction pipe 104 is effective to supply the plating liquid uniformly to the surface, to be plated, if the plating liquid introduction pipe 104 is of a manifold structure. Specifically, the plating liquid introduction pipe 104 has a plating liquid introduction passage 104a extending continuously in its longitudinal direction, and a plurality of plating liquid introduction ports 104b spaced at a given pitch along the plating liquid introduction passage 104a and extending downwardly therefrom in communication therewith. The anode 98 has a plurality of plating liquid supply ports 98a defined therein at positions corresponding to the plating liquid introduction ports 104b. The anode 98 also has a number of vertically extending through holes 98b defined therein over its entire region. The plating liquid that is introduced from the plating liquid supply pipe 102 into the plating liquid introduction pipe 104 flows through the plating liquid introduction ports 104b and the plating liquid supply ports 98a to a plating space 99 (see FIG. 17) formed between the anode 98 and the substrate W. The plating liquid discharge pipe 106 is evacuated to discharge the plating liquid within the plating space 99 formed between the anode 98 and the substrate W via the through holes 98b and the suction chamber 100 from the plating liquid discharge pipe 106.

[0054] Further, a liquid supply pipe 120 for separately introducing a solution or plating liquid, having a different additive concentration from the plating liquid, into the plating space 99 formed between the anode 98 and the substrate W is connected to the housing 94. By introducing, during a plating process, the solution or plating liquid having a different additive concentration into the plating space 99 from the liquid supply pipe 120, the change of additive concentration

in the plating liquid contained in the plating space 99 can arbitrarily be controlled.

**[0055]** As shown in FIG. 17, the anode 98 is designed to have substantially the same size (diameter) as the substrate W so that the anode covers substantially the whole surface of the substrate W.

**[0056]** In order to suppress the generation of slime, the anode 98 is made of copper containing 0.03 to 0.05 % of phosphorus (phosphorus copper). When the anode 98 is made of phosphorus copper, a black film is formed on the surface of the anode 98 as the plating process progresses. The black film is made of a  $\text{Cu}^+$  complex containing phosphorus and Cl, and comprises  $\text{Cu}_2\text{Cl}_2 \cdot \text{Cu}_2\text{O} \cdot \text{Cu}_3\text{P}$ , etc. Since the black film suppresses a copper disproportionation reaction, it is important to stably form the black film on the surface of the anode 98 for the purpose of stabilizing the plating process. However, if the black film is dried and oxidized, and peeled off the anode 98, then it tends to produce particles and causes to change the composition of the plating.

**[0057]** In this embodiment, a plating liquid impregnation material 110 comprising a water retaining material and covering the entire surface of the anode 98 is attached to the lower surface of the anode 98. The plating liquid impregnation material 110 is impregnated with the plating liquid to wet the surface of the anode 98, thereby preventing a black film from falling onto the plated surface of the substrate by drying, and oxidizing, and simultaneously facilitating escape of air to the outside when the plating liquid is poured between the surface, to be plated, of the substrate and the anode 98.

**[0058]** Further, by thus attaching the plating liquid impregnation material 110 to the anode 98 and contacting the material 110 with the plating liquid poured into the plating space 99 between the surface, to be plated, of the substrate W and the anode 98, a particular additive component, e.g. a leveler, can be adsorbed and removed by the plating liquid impregnation material 110. The use of the plating liquid impregnation material is thus effective for reducing the lever concentration of the plating liquid in the plating space 99.

**[0059]** The plating liquid impregnation material 110 has both functions of retaining liquid and passing liquid there-through, and has excellent chemical resistance. Specially, the plating liquid impregnation material 110 has endurance against an acid plating liquid including sulfuric acid having high concentration. The plating liquid impregnation material 110 comprises, for example, a woven fabric of polypropylene to prevent elution of the impurity in the sulfuric acid solution from having a bad influence to the plating efficiency (plating speed, resistivity and filling characteristics). The plating liquid impregnation material 110 may comprises at least one material of polyethylene, polyester, polyvinyl chloride, Teflon, polyvinyl alcohol, polyurethane, and derivatives of these materials, other than polypropylene. Nonwoven fabric or sponge-like structure may use in place of woven fabric. Porous ceramics and sintered polypropylene made of Alumina and SiC and the like are available.

**[0060]** That is, many fixing pins 112 each having a head portion at the lower end are arranged such that the head portion is provided in the plating liquid impregnation material 110 so as not to be releasable upward and a shaft portion of the fixing pin pierces the interior of the anode 98, and the fixing pins 112 are urged upward by U-shaped plate springs 114, whereby the plating liquid impregnation material 110 is brought in close contact with the lower surface of the anode 98 by the resilient force of the plate springs 114 and is attached to the anode 98. With this arrangement, even when the thickness of the anode 98 gradually decreases with the progress of plating, the plating liquid impregnation material 110 can be reliably brought in close contact with the lower surface of the anode 98. Thus, it can be prevented that air enters between the lower surface of the anode 98 and the plating liquid impregnation material 110 to cause poor plating.

**[0061]** Incidentally, columnar pins made of PVC (polyvinyl chloride) or PET and having a diameter of, for example, about 2 mm may be arranged from the upper surface side of the anode so as to pierce the anode, and an adhesive may be applied to the front end surface of each of the pins projecting from the lower surface of the anode to fix the anode to the plating liquid impregnation material. When the plating liquid impregnation material has a sufficient strength such as a ceramics, the anode may be placed on the plating liquid impregnation material fixed to the supporter without using pins for fixing the impregnated material. It is not necessary to bring in close contact the plating impregnation material with the anode, and a plating liquid may be filled into a gap between the plating impregnation material and the anode.

**[0062]** When the substrate holder 36 is in the plating position B (see FIG. 5), the electrode head 28 is lowered until the gap between the substrate W held by the substrate holder 36 and the plating liquid impregnation material 110 becomes about 0.5 to 3 mm, for example. Then, the plating liquid is supplied from the plating liquid supply pipe 102 to fill the gap between the upper surface, to be plated, of the substrate W and the anode 98 while impregnating the plating liquid impregnation material 110 with the plating liquid, thus plating the upper surface of the substrate W.

**[0063]** As shown in FIG. 4, stopper bars 116 are erected outwardly of the support columns 84 supporting the cathode portion 38. Protrusions 96a provided on the periphery of the support frame 96 are brought into contact with the upper surfaces of the stopper bars 116, whereby the descent of the electrode portion 28 is controlled.

**[0064]** A plating process carried out by the substrate plating apparatus according to the above embodiment will be described below.

**[0065]** First, a substrate W, to be plated, is taken out from one of the loading/unloading units 10 by the transfer robot 14, and transferred, with the surface, to be plated, being oriented upwardly, through the substrate carry-in and carry-out opening 50 defined in the side panel, into one of the plating units 12. At this time, the substrate holder 36 is in the



lower substrate transfer position A. After the hand of the transfer robot 14 has reached a position directly above the substrate stage 68, the hand of the transfer robot 14 is lowered to place the substrate W on the support arm 70. The hand of the transfer robot 14 is then retracted through the substrate carry-in and carry-out opening 50.

[0066] After the hand of the transfer robot 14 is retracted, the cup 40 is elevated. Then, the substrate holder 36 is lifted from the substrate transfer position A to the pre-treating/cleaning position C. As the substrate holder 36 ascends, the substrate W placed on the support arms 70 is positioned by the positioning plate 72 and the pressing finger 74 and then reliably gripped by the fixing fingers 76.

[0067] On the other hand, the electrode head 28 of the electrode arm 30 is in a normal position over the plating liquid tray 22 now, and the plating liquid impregnation material 110 or the anode 98 is positioned in the plating liquid tray 22. At the same time that the cup 40 ascends, the plating liquid starts being supplied to the plating liquid tray 22 and the electrode head 28. Until the step of plating the substrate W is initiated, the new plating liquid is supplied, and the plating liquid discharge pipe 106 is evacuated to replace the plating liquid in the plating liquid impregnation material 110 and remove air bubbles from the plating liquid in the plating liquid impregnation material 110. When the ascending movement of the cup 40 is completed, the substrate carry-in and carry-out opening 50 in the side panel is closed by the cup 40, isolating the atmosphere in the side panel and the atmosphere outside of the side panel from each other.

[0068] When the cup 40 is elevated, the pre-coating step is initiated. Specifically, the substrate holder 36 that has received the substrate W is rotated, and the pre-coating/recovering arm 32 is moved from the retracted position to a position confronting the substrate W. When the rotational speed of the substrate holder 36 reaches a setting value, the pre-coating nozzle 64 mounted on the tip end of the pre-coating/recovering arm 32 intermittently discharges a pre-coating liquid which comprises a surface active agent, for example, toward the surface to be plated of the substrate W. At this time, since the substrate holder 36 is rotating, the pre-coating liquid spreads all over the surface, to be plated, of the substrate W. Then, the pre-coating/recovering arm 32 is returned to the retracted position, and the rotational speed of the substrate holder 36 is increased to spin the pre-coating liquid off and dry the surface, to be plated, of the substrate W.

[0069] After the completion of the pre-coating step, the plating step is initiated. First, the substrate holder 36 is stopped against rotation, or the rotational speed thereof is reduced to a preset rotational speed for plating. In this state, the substrate holder 36 is lifted to the plating position B. Then, the peripheral edge of the substrate W is brought into contact with the cathode electrodes 88, when it is possible to cause an electric current to flow, and at the same time, the sealing member 90 is pressed against the upper surface of the peripheral edge of the substrate W, thus sealing the peripheral edge of the substrate w in a water-tight fashion.

[0070] Based on a signal indicating that the pre-coating step for the loaded substrate W is completed, the electrode arm 30 is swung in a horizontal direction to displace the electrode head 28 from a position over the plating liquid tray 22 to a position over the plating position. After the electrode head 28 reaches this position, the electrode head 28 is lowered toward the cathode portion 38. At this time, the plating liquid impregnation material 110 does not contact with the surface, to be plated, of the substrate W, but is held closely to the surface, to be plated, of the substrate W at a distance ranging from 0.5 mm to 3 mm. When the descent of the electrode head 28 is completed, a plating current is supplied, and the plating liquid is supplied from the plating liquid supply pipe 102 into the electrode head 28, and then from the plating liquid supply ports 98a through the anode 98 to the plating liquid impregnation material 110.

[0071] When the supply of the plating liquid continues, the plating liquid containing copper ions, which has seeped out of the plating liquid impregnation material 110, is filled into the gap between the plating liquid impregnation material 110 and the surface, to be plated, of the semiconductor substrate W so that copper plating is performed on the surface, to be plated, of the substrate.

[0072] After supplying a predetermined amount of the plating liquid, the introduction of the plating liquid is stopped, and the substrate holder 36 is rotated at a low speed so that the plating liquid can be supplied evenly to the surface, to be plated, of the substrate. The rotation of the substrate holder is continued e.g. for 5 minutes. The plating liquid used in this embodiment contains an additive concentration of e.g. 1.0 mL/L, and it is used in an amount of e.g. 50mL according to the volume of the plating space 99. The additive concentration decreases with the progress of the plating process, whereby the unevenness in the plated film thickness between the interconnection region and the non-interconnection region is corrected.

[0073] More specifically, in the course of plating of the substrate, the additive concentration gradually decreases with the progress of plating due to the take-in of the additive within the deposited metal film and the oxidation degradation at the anode. The change (decrease) of additive concentration in the plating liquid contained in the plating space 99 formed between the substrate and the anode is large in such cases as this embodiment where the plating of the substrate is by the close-to-anode plating where the amount of the plating liquid itself in the plating space 99 is small, and the introduction of the plating liquid into the plating space 99 is conducted only before plating, and not conducted during the plating process. This effectively corrects the unevenness in the plated film thickness between the interconnection region and the non-interconnection region. Further, the use of the plating liquid impregnation material can adsorb and remove a particular additive compound, e.g. a leveler, thereby more effectively reducing the leveler con-

centration of the plating liquid contained in the plating space.

**[0074]** Though in this embodiment the introduction of the plating liquid into the plating space 99 is conducted only before the plating process (batch-wise introduction), the plating liquid may be introduced intermittently during the plating process. Further, by separately introducing, during the plating process, the solution or plating liquid having a different additive concentration into the plating space 99 from the liquid supply pipe 120, the change of additive concentration in the plating liquid contained in the plating space 99 can be made larger.

**[0075]** When the plating treatment is completed, the electrode arm 30 is raised and then swung to return to the position above the plating liquid tray 22 and to lower to the ordinary position. Then, the pre-coating/recovering arm 32 is moved from the retreat position to the position confronting to the semiconductor substrate W, and lowered to recover the remainder of the plating liquid on the substrate W by a plating liquid recovering nozzle 66. After recovering of the remainder of the plating liquid is completed, the pre-coating/recovering arm 32 is returned to the retreat position, and pure water is supplied from the fix nozzle 34 for supplying pure water toward the central portion of the substrate W for rinsing the plated surface of the substrate. At the same time, the substrate holder 36 is rotated at an increased speed to replace the plating liquid on the surface of the substrate W with pure water. Rinsing the substrate W in this manner prevents the splashing plating liquid from contaminating the cathode electrodes 88 of the cathode portion 38 during descent of the substrate holder 36 from the plating position B.

**[0076]** After completion of the rinsing, the washing with water step is initiated. That is, the substrate holder 36 is lowered from the plating position B to the pre-treatment/cleaning position C. Then, while pure water is supplied from the fixed nozzle 34 for supplying pure water, the substrate holder 36 and the cathode portion 38 are rotated to perform washing with water. At this time, the seal member 90 and the cathode electrodes 88 can also be cleaned, simultaneously with the substrate W, by means of pure water directly supplied to the cathode 38, or pure water scattered from the surface of the substrate W.

**[0077]** After washing with water is completed, the drying step is initiated. That is, supply of pure water from the fixed nozzle 34 is stopped, and the rotational speed of the substrate holder 36 and the cathode portion 38 is further increased to remove pure water on the surface of the substrate W by centrifugal force and to dry the surface of the substrate W. The seal member 90 and the cathode electrodes 88 are also dried at the same time. Upon completion of the drying, the rotation of the substrate holder 36 and the cathode portion 38 is stopped, and the substrate holder 36 is lowered to the substrate transfer position A. Thus, the gripping of the substrate W by the fixing fingers 76 is released, and the substrate W is just placed on the upper surfaces of the support arms 70. At the same time, the cup 40 is also lowered.

**[0078]** All the steps including the plating step, the pre-treating step accompanying to the plating step, the cleaning step, and the drying step are now finished. The transfer robot 14 inserts its hand through the substrate carry-in and carry-out opening 50 into the position beneath the substrate W, and raises the hand to receive the processed substrate W from the substrate holder 36. Then, the transfer robot 14 returns the processed substrate W received from the substrate holder 36 to one of the loading/unloading units 10.

**[0079]** This embodiment shows the case where the plating is carried out at a constant temperature. In this case, though the additive concentration of the plating liquid decreases until the plating liquid impregnation material reaches the adsorption saturation, this effect can no longer be expected after the adsorption saturation. Accordingly, for example, device for adjusting the temperature of the plating liquid during the plating process, such as a heater, may be provided around the anode so as to gradually raise the plating temperature in accordance with the progress of the plating process, whereby the adsorption capacity of the plating liquid impregnation material for the additive in the plating liquid can be enhanced. It is also possible to utilize spontaneous temperature rising due to Joule heat that generates during the plating process. In this case, after the completion of plating, the plating liquid impregnation material may be brought into contact with a low-temperature plating liquid to detach part of the adsorbed additive. The additive excessively adsorbed due to the high temperature can thus be detached.

**[0080]** Further, the plating apparatus may be arranged such that a plurality of plating liquids having different additive concentrations can be introduced, through the plating liquid supply pipe 102, into the space between the surface, to be plated, of the substrate and the anode. Plating may be conducted by using, at the initial stage of the plating process, a plating liquid having a proper additive concentration for the metal filling into interconnection, and changing the plating liquid with other plating liquids having a lower additive concentration at the middle or later stage of the plating process, thereby adjusting the additive concentration of the plating liquid during the plating process.

**[0081]** Adjustment of the additive concentration during the plating process may also be made by using, at the initial stage of the plating process, an anode that holds a plating liquid impregnation material impregnated with a plating liquid having a proper additive concentration for the metal filling, and using, at the middle or later stage of the plating process, an anode that holds a plating liquid impregnation material impregnated with a plating liquid having a lower additive concentration.

**[0082]** The following are the results of various experiments which were conducted to show the technical effects attained by the plating treatment according to this embodiment.

**[0083]** First, in order to examine the relationship between the amount of plating liquid and the filling properties, plating

## EP 1 191 128 A2

was conducted with various amounts of plating liquid under the following plating conditions to determine the additive concentration at the initial, middle and later stages of the plating process, the film-thickness difference between the interconnection and non-interconnection regions, and the presence or absence of voids in interconnection. The results are shown in Table 1. Plating conditions:

- \* Copper sulfate pentahydrate = 225 g/L,  
Sulfuric acid = 55 g/L, Chloride ion = 60 mg/L,  
Additive = DMEC#40 (all manufactured by EBARA-UDYLITE CO., LTD.)
- \* Temperature = 25°C, Electric current density = 20 mA/cm<sup>2</sup>,  
Plating time = 5 min (average thickness of plated film: 2000 nm)
- \* Impregnation material : not used

(Table 1)

Amount of plating liquid and filling properties						
Amount of Plating liquid (ml/substrate)		5ml	50ml	500 ml	1000 ml	5000 ml
Measured additive concentration (ml/l)	Initial stage (0min)	1.0	1.0	1.0	1.0	1.0
	Middle stage (2.5min)	0	0	0.6	0.9	1.0
	Later stage (5min)	0	0	0.1	0.5	0.9
Film-thickness difference (nm)	(=Interconnection region Non-interconnection region)	0	100	400	1000	1800
Presence of voids in interconnection		Found	None	None	None	None

[0084] As can be seen from Table 1, the use of a smaller amount of plating liquid results in a smaller difference in film thickness of the plated film between the interconnection region and the non-interconnection region, thus providing a film-thickness distribution feasible for CMP processing. This is considered to be due to decrease in the brightener component which is the main cause of the film-thickness difference. Table 1 also shows that the use of an extremely small amount of plating liquid results in the formation of voids in the interconnection, and thus is not preferred. This may be due to shortage of the brightener component which is the main factor for the bottom-up growth in via holes important for the metal filling into fine interconnection.

[0085] Next, in order to examine the change of additive concentration with or without the use of a plating liquid impregnation material, plating was conducted under the following plating conditions to determine the additive concentration at the initial, middle and later stages of the plating process, the film-thickness difference between the interconnection and non-interconnection regions, and the presence or absence of voids in interconnection. The results are shown in Table 2.

Plating conditions:

[0086]

- \* Copper sulfate pentahydrate = 225 g/L,  
Sulfuric acid = 55 g/L, Chloride ion = 60 mg/L,  
Additive = DMEC#40 (all manufactured by EBARA-UDYLITE CO., LTD.)
- \* Temperature = 25°C, Electric current density = 20 mA/cm<sup>2</sup>,  
Plating time = 5 min (average thickness of plated film: 2000 nm)
- \* Impregnation material : PVA sponge (thickness: 4 mm), previous additive-adsorption treatment not made
- \* Amount of plating liquid : 1000 mL/substrate

(Table 2)

Additive adjustment by adsorption by impregnation material			
		With impregnation material	Without impregnation material
Measured additive concentration (ml/l)	Initial stage (0min)	1.0	1.0
	Middle stage (2.5min)	0.2	0.9
	Later stage (5min)	0	0.5
Film-thickness difference (nm)	(=Interconnection region Non-interconnection region)	100-150	1000
Presence of voids in interconnection		None	None

[0087] As can be seen from Table 2, by carrying out plating in the presence of a plating liquid impregnation material having additive-adsorbing properties, the additive concentration can be effectively decreased during the plating process, whereby plating can be achieved with a smaller film-thickness difference and without formation of voids in the interconnection. This is considered to be due to the fact that the concentration of the brightener, which is necessary for the interconnection filling, is high at the initial stage of the plating process, whereas at the middle or later stage of the plating process, the brightener concentration is lowered by adsorption by the plating liquid impregnation material.

[0088] Further, multistage plating using plating liquids having different additive concentrations and normal plating using single plating liquid were conducted under the following plating conditions to determine the additive concentration at the initial, middle and later stages of the plating process, the film-thickness difference between the interconnection and non-interconnection regions and the presence or absence of voids in interconnection. The results are shown in Table 3.

Plating conditions:

[0089]

- \* Copper sulfate pentahydrate = 225 g/L,  
Sulfuric acid = 55 g/L, Chloride ion = 60 mg/L,  
Additive = DMEC#40 (all manufactured by EBARA-UDYLITE CO., LTD.)
- \* Temperature = 25°C, Electric current density = 20 mA/cm<sup>2</sup>,  
Plating time = 5 min (average thickness of plated film: 2000 nm)
- \* Impregnation material : not used
- \* Amount of plating liquid : 5000 mL/substrate, the additive concentration shown in Table 3

(Table 3)

Results of multistage plating			
		Multistage plating(ml/l) 0 - 1.5min: Concentration 1.0 1.5 - 3min: Concentration 0.3 3 - 5min: Concentration 0	Normal(Single liquid) Concentration: 1.0ml/l
Measured additive concentration(ml/l)	Initial stage (0min)	1.0	1.0
	Middle stage (2.5min)	0.3	1.0
	Later stage (5min)	0	0.9

(Table 3) (continued)

Results of multistage plating			
		Multistage plating(ml/l) 0 - 1.5min: Concentration 1.0 1.5 - 3min: Concentration 0.3 3 - 5min: Concentration 0	Normal(Single liquid) Concentration: 1.0ml/l
Film thickness difference (nm)	(=Interconnection region Non-interconnection region)	100-150	1800
Presence of voids in interconnection		None	None

[0090] As can be seen Table 3, by decreasing stepwise the additive concentration of a plating liquid in accordance with the progress of the plating process, a plated film having a small film-thickness difference, thus feasible for CMP processing, can be obtained.

[0091] As described hereinabove, according to this embodiment of the present invention, plating of a substrate can be performed with a small film-thickness difference between the interconnection and non-interconnection regions, which is feasible for a later CMP processing, and without forming voids in the interconnection. This improves the product yield, can simplify the process steps and attains a considerable lowering of the production cost.

[0092] FIGS. 21 and 22 show a plating apparatus according to the second embodiment of the present invention. FIG. 21 is a longitudinal sectional front view of an electrode arm containing a substrate holder, and FIG. 22 is a plan view showing the relationship between a substrate and an anode.

[0093] According to the plating apparatus of this embodiment, the size (diameter) of the anode 98 is designed to be smaller than the size (diameter) of the substrate W, so that the area of the anode 98 becomes smaller than the area of the substrate W. Further, a rotary motor 130 as an anode-rotating device is provided at the upper end of the electrode portion 28, so that the anode 98 is allowed to rotate by the rotary motor 130. The other construction of the apparatus is substantially the same as the above described plating apparatus according to the first embodiment.

[0094] As described above, when a plating current flows, the electric current value on the inner central side of the substrate is smaller than the electric current value on the outer peripheral side due to the difference in the sheet resistance of the substrate W. If the energization time of the plating current can be made longer on the inner central side of the substrate W than the outer peripheral side, it becomes possible to make the product of the electric current value and the energization time substantially equal to the inner central side and the outer peripheral side of the substrate W. Since the film thickness of the plated film formed on the surface of the substrate W is proportional to the product of the electric current value of the plating current and the energization time of the plating current, making the product equal as described above can provide a plated film having a uniform film thickness over the entire surface of the substrate.

[0095] According to the plating apparatus of this embodiment, adjustment of the energization time of the plating current, which realizes the formation of a plated film having a uniform film thickness, is made by making the area of the anode 98 smaller than the area of the substrate W, and by driving the rotary motor 46 as a substrate-rotating device (see FIG. 4) to rotate the substrate holder 36 together with the substrate W during the plating process. Thus, when the substrate W is rotated, the point P1 shown in FIG. 22, situated on the inner central side of the substrate, always faces the anode 98 and causes the electric current to flow through. On the other hand, in the case of the point P2 situated on the outer peripheral side of the substrate, it faces the anode 98 when it moves (rotates) along the solid line F, but it does not face the anode 98 and the electric current does not flow therethrough when it moves (rotates) along the broken line G. Accordingly, the energization time of the electric current becomes longer at the point P1 than the point P2.

[0096] According to this embodiment, the energization time of the electric current on the inner central side of the substrate W is thus made longer than that on the outer peripheral side by properly selecting the shape, size, area and positioning of the anode 98 and also the rotational speed of the substrate W, thereby making the product of the plating current value and the energization time of the plating current equal over the entire surface of the substrate W, whereby a plated film having a uniform film thickness can be formed. In addition, since the area of the anode 98 is made smaller than the area of the substrate W, it becomes possible to utilize the surface of the substrate W not facing the anode 98, i.e. the exposed surface of the substrate, to conduct an optical film-thickness measurement or the like simultaneously

with the formation of the plated film.

[0097] The area of the anode 98 is selected, as described above, so that the film thickness of the plated film may be made uniform over the entire surface of the substrate, and is preferably selected from the range of 25-95 % of the area of the substrate W. When the anode 98 is in a disc shape, if the area of the anode 98 is less than 25 % of the area of the substrate, i.e. the diameter of the anode 98 is smaller than the radius of the substrate W, there should be a portion in the vicinity of the center of the substrate W that cannot be plated. The rotational speed of the substrate W is preferably 3-60 revolutions per minute, more preferably 5-40 revolutions per minute.

[0098] The plating treatment may be carried out while rotating the anode 98 by driving the rotary motor 130 as an anode-rotating device. Alternatively, plating may be carried out while the rotary motor 130 is stopped and the anode 98 is kept stationary. When plating is conducted while rotating the anode 98, the rotating direction of the anode 98 may be the same as or opposite to the rotating direction of the substrate W; however, it is preferred to rotate the anode 98 in the same direction as the substrate. The rotational speed of the anode is preferably 3-60 revolutions per minute, more preferably 5-40 revolutions per minute.

[0099] The anode 98 may be in any shape insofar as the uniform plated film thickness over the entire substrate surface can be obtained, and can be, for example, in an oval or heart-like shape.

[0100] FIG. 23 is a plan view of the electrode arm 30 of the plating apparatus according to the third embodiment of the present invention. The construction of the plating apparatus of this embodiment is fundamentally the same as the above plating apparatus according to the second embodiment. A groove 130a is formed along the length of the electrode portion 30 of this apparatus. Further, the rotary motor 130 as an anode-rotating device mounted on the upper end of the electrode portion 28 is designed to function also as an anode-translating device. Thus, by the actuation of the rotary motor 130, the anode 98 can translate in the direction of arrow H shown in FIG. 24. Since the other construction is the same as the apparatuses of the above described embodiments, the description thereof is herein omitted.

[0101] While the plating apparatus of this embodiment operates in the same manner as the plating apparatus of the second embodiment, in the case of this apparatus, simultaneously with rotating of the substrate W by the rotary motor 64 (see FIG. 4) during the plating process, the anode 98 is translated in the direction of arrow H, shown in FIG. 23, by the rotary motor 130 that functions also as an anode-translating device. The translational speed of the anode 98 is preferably 5-40 reciprocations per minute.

[0102] Though the above-described second and third embodiments show the case where the substrate-rotating device allows the substrate to rotate about its central axis, the device may be designed to allow the substrate to revolve eccentrically. It is also possible to design the substrate-rotating device so that the device itself can make a scroll movement relative to the anode.

[0103] FIG. 25 is a pattern diagram illustrating the relationship between the substrate W and the electrode portion 28 of the plating apparatus according to the fourth embodiment of the present invention.

[0104] Though the construction of the plating apparatus of this embodiment is fundamentally the same as the above-described apparatuses, it differs in that the anode 98 of the electrode portion 28 is made inclined relative to the substrate W, as shown in FIG. 25. Since the other construction of this apparatus is the same as the above-described first embodiment, the description thereof is herein omitted.

[0105] As shown in FIG. 25, the anode 98 is made inclined so that the distance between the anode and the substrate W is small on the inner central side of the substrate W and large on the outer peripheral side of the substrate W. The angle of inclination, i.e. the angle  $\alpha$  shown in FIG. 25, is preferably not more than  $30^\circ$ . By inclining the anode 98 in this manner, the resistance R2 of the plating liquid, described above referring to FIG. 30, is made smaller on the inner central side of the substrate and larger on the outer peripheral side of the substrate, whereby the electric current value is made more equal on the inner central side of the substrate to the outer peripheral side. Thus, in addition to the adjustment of the energization time of the plating current according to the second embodiment, the electric current values at various points of the substrate can also be adjusted, thereby making the product of the time for passing electric current and the electric current value equal over the entire surface of the substrate, whereby the film thickness of the plated film formed on the substrate W can be made uniform over the entire surface of the substrate W.

[0106] Preferably, the minimum distance between the anode 98 and the substrate W, i.e. the distance between the anode and the central portion of the substrate W, is in the range 2-65 mm. The plating liquid impregnation material 110 should preferably have a thickness of 2-15 mm. It is also possible to make the size of the anode 98 substantially the same as the substrate W, and design the combination of the anode 98 and the plating liquid impregnation material 110 as shown in FIG. 26, viz. a symmetrical configuration about the central axis of the substrate. In this case, the above-described adjustment of the energization time of the electric current is not necessary, and the formation of a plated film having a uniform film thickness can be achieved merely by the adjustment of electric current value.

[0107] FIG. 27A is a pattern diagram illustrating the relationship between the substrate and the anode at the initiation of the plating process in the plating apparatus according to the fifth embodiment of the present invention, and FIG. 27B is a pattern diagram illustrating the relationship between the substrate and the anode at the completion of the plating process in the plating apparatus according to the fifth embodiment of the present invention. FIG. 28A and FIG.

28B are equipotential diagrams showing the state of electric field between the anode 98 and the substrate W in the relationships of FIG. 27A and FIG. 27B, respectively.

[0108] Though the construction of the plating apparatus of this embodiment is basically the same as the above-described first embodiment, it differs in that the motor 54 (see FIGS. 8 and 9) for vertically movement functions as means for changing the distance between the anode 98 and the substrate W (as a pulling-away device), as shown in FIGS. 27A and 27B.

[0109] While the plating apparatus of this embodiment operates in the same manner as the plating apparatus of the first embodiment, in the case of this apparatus, the distance between the anode 98 and the substrate W is changed, during the period between the initiation of plating (FIG. 27A) and the completion of plating (FIG. 27B), by the motor 54 as a pulling-away device. Thus, at the initiation of plating (FIG. 27A), the distance between the anode 98 and the substrate W is set preferably in the range of 2-18 mm. While keeping this distance, a plated film with a thickness of about 100 nm is formed on the surface of the substrate W. Thereafter, the plating treatment is continued while the distance between the anode 98 and the substrate W is made larger by pulling the electrode portion 28 upward by the motor 54. The plating treatment is completed when a desired plated film thickness is obtained (FIG. 27B). The distance between the anode 98 and the substrate W is preferably in the range of 3-50 mm.

[0110] Since the distance between the anode 98 and the substrate W is small at the initiation of plating, the potential gradient is higher on the inner central side of the substrate W than the outer peripheral side, as shown in FIG. 28A. Accordingly, the electric current value is higher on the inner central side of the substrate W than the outer peripheral side, whereby a larger amount of plated film is formed on the inner central side of the substrate W. When a plated film is thus formed on the surface of the substrate W, the sheet resistance value at the portion of the substrate where the plated film is formed in a larger amount, i.e., the inner central portion of the substrate W, becomes lower. If the plating is still continued, the plated film becomes much more thicker on the inner central side of the substrate. In view of the above, the distance between the anode 98 and the substrate W is made larger, during the plating process, according to this embodiment.

[0111] When the distance between the anode 98 and the substrate W is made larger, as shown in FIG. 28B, the potential gradient on the outer peripheral side of the substrate W becomes higher than the inner central side, whereby the electric current value becomes larger on the outer peripheral side of the substrate W than the inner central side. Thus, contrary to the case of FIG. 28A, a larger amount of plated film is formed on the outer peripheral side of the substrate W. Therefore, as the result of transition from the state of FIG. 27A to the state of FIG. 27B, in accordance with this embodiment, the film thickness of the plated film can be finally made uniform over the entire surface of the substrate.

[0112] When the electrode portion 28 is pulled upward, it may be pulled up slowly, taking a considerable time, or quickly at a stretch.

[0113] The embodiments of the present invention as hereinabove described are but illustrative examples, and the present invention is not limited thereto. It will be understood that many changes and modifications may be made to the above embodiments without departing from the spirit of the present invention. It will, therefore, be understood that the above-described embodiments, in combinations thereof, may be practiced within the scope of the present invention.

[0114] Though plating apparatuses of a substrate-immersing type, in which plating and treatments incidental thereto can be conducted in a single unit, are described hereinabove, the present invention is not limited to such type but applicable to any types of plating apparatuses, including a face-down type and a face-up type. As an example, a plating apparatus of a face-down type, to which the seventh embodiment of the present invention is applied, is shown in FIG. 29.

[0115] The plating apparatus shown in FIG. 29 has a substrate holder 200 for detachably holding a substrate W with its surface, to be plated, facing downward. A disc-shaped anode 202 (having a smaller size than the substrate W), which is eccentric to the substrate W, is disposed at the bottom of a substantially cylindrical plating tank 201. A rotary motor 203 as an anode-rotating device is provided beneath the anode 202. Further, a rotary motor 205 as a substrate-rotating device is mounted on the upper portion of a frame 204 that supports the substrate holder 200. By thus providing the anode-rotating device 203 and the substrate-rotating device 205, it becomes possible, as with the above-described plating apparatuses of a substrate-immersing type, to make the energization time of an electric current on the inner central side of the substrate W longer than that on the outer peripheral side, whereby a plated film having a uniform film thickness can be formed.

[0116] As described hereinabove, according to the present invention, the portion of a substrate facing an anode is moved in such a state that the inner central portion of the surface of the substrate faces the anode for a longer time than the outer peripheral portion of the surface of the substrate faces the anode, thereby making the energization time of the plating current to the inner central portion of the substrate longer than the energization time of the plating current to the outer peripheral portion, whereby the products of the electric current values and the energization times of the electric current at various points of the substrate can be made equal over the entire surface of the substrate. Consequently, it becomes possible to make the film thickness of the plated film formed on the substrate uniform over the entire surface of the substrate.

[0117] Further, by making the distance between the anode and the inner central portion of the substrate smaller than the distance between the substrate and the outer peripheral portion of the substrate, the resistance of a plating liquid can be made smaller at the inner central portion of the substrate and larger at the outer peripheral portion. This can make the electric current value more equal at the inner central portion of the substrate to at the outer peripheral portion, whereby the film thickness of the plated film formed on the substrate can be made uniform over the entire surface of the substrate.

[0118] Further according to the present invention, the distance between the substrate and the anode can be changed after the initiation of plating. Since the potential gradient is higher on the inner central side of the substrate than the outer peripheral side at the initiation of plating, a larger amount of plated film is formed on the inner central side. This situation can be reversed by later making the distance between the anode and the substrate larger, whereby a plated film having a uniform film thickness over the entire surface of the substrate can be obtained.

[0119] The above and other objects, features, and advantages of the present invention will be apparent from the following description when taken in conjunction with the accompanying drawings which illustrates preferred embodiments of the present invention by way of example.

## Claims

### 1. A plating method, comprising:

filling a plating liquid containing metal ions and an additive into a plating space formed between a substrate and an anode disposed closely to the substrate so as to face the substrate; and  
changing the concentration of the additive in the plating liquid filled into said plating space during a plating process.

2. The plating method according to claim 1, wherein the concentration of the additive in the plating liquid is adjusted by intermittently supplying the plating liquid into said plating space.

3. The plating method according to claim 1, wherein the concentration of the additive in the plating liquid is adjusted by supplementary addition of the additive to said plating space.

4. The plating method according to claim 1, wherein the concentration of the additive in the plating liquid is adjusted by removal of the additive in the plating liquid.

5. The plating method according to claim 1, wherein the additive is a brightener, and the concentration of the brightener at the middle and later stages of the plating process is lower than that at the initial stage of the plating process.

6. The plating method according to claim 1, wherein the additive is a leveler, and the concentration of the leveler at the middle and later stages of the plating process is higher than that at the initial stage of the plating process.

### 7. A plating apparatus, comprising:

a substrate holder for holding a substrate so that a current can flow from a cathode to the substrate;  
an anode opposed to the substrate held by said substrate holder; and  
a plating liquid introducing device for introducing a plating liquid into a plating space formed between the substrate and said anode in a batch process or an intermittent process.

8. The plating apparatus according to claim 7, wherein a plating liquid impregnation material is provided in said plating space.

9. The plating apparatus according to claim 7, further comprising a liquid introducing device for introducing into said plating space a liquid having a different additive concentration from the additive concentration of the plating liquid.

10. The plating apparatus according to claim 9, wherein a plating liquid impregnation material is provided in said plating space.

11. The plating apparatus according to claim 7, further comprising a temperature adjusting device for adjusting the temperature of the plating liquid in said plating space.



12. A plating apparatus, comprising:

a substrate holder for holding a substrate so that a current can flow from a cathode to the substrate;  
 an anode opposed to the substrate held by said substrate holder; and  
 a moving device for moving a portion of the substrate facing said anode in such a state that an inner central  
 portion of the surface of the substrate faces said anode for a longer time than an outer peripheral portion of  
 the surface of the substrate faces said anode.

13. The plating apparatus according to claim 12, wherein said moving device comprises a substrate-rotating device  
 for rotating the substrate.

14. The plating apparatus according to claim 12, wherein said moving device comprises an anode-rotating device for  
 rotating said anode.

15. The plating apparatus according to claim 12, wherein said moving device comprises an anode-translating device  
 for translating said anode.

16. A plating apparatus, comprising:

a substrate holder for holding a substrate so that a current can flow from a cathode to the substrate; and  
 an anode opposed to the substrate held by said substrate holder,

wherein the distance between said anode and an inner central portion of the substrate is smaller than the  
 distance between said anode and an outer peripheral portion of the substrate.

17. A plating apparatus, comprising:

a substrate holder for holding a substrate so that a current can flow from a cathode to the substrate;  
 an anode opposed to the substrate held by said substrate holder; and  
 a distance changing device for changing the distance between the substrate and said anode after initiation of  
 plating.

18. A plating method, comprising:

disposing a substrate and an anode in such a state that the substrate faces said anode;  
 flowing a current between the substrate and said anode while supplying a plating liquid therebetween; and  
 moving a portion of the substrate facing said anode in such a state that an inner central portion of the surface  
 of the substrate faces said anode for a longer time than an outer peripheral portion of the surface of the  
 substrate faces said anode.

19. The plating method according to claim 18, wherein the portion of the substrate facing said anode is moved by  
 rotation of the substrate.

20. The plating method according to claim 18, wherein the portion of the substrate facing said anode is moved by  
 rotation of said anode.

21. The plating method according to claim 18, wherein the portion of the substrate facing said anode is moved by  
 translation of said anode.

22. A plating method, comprising:

disposing a substrate and an anode so that the substrate faces said substrate; and  
 flowing a current between the substrate and said anode while supplying a plating liquid therebetween,

wherein the distance between said anode and an inner central portion of the substrate is smaller than the  
 distance between said anode and an outer peripheral portion of the substrate.

23. A plating method, comprising:

## EP 1 191 128 A2

disposing a substrate and an anode so that the substrate faces said anode;  
flowing a current between the substrate and said anode while supplying a plating liquid therebetween; and  
changing the distance between the substrate and said anode after initiation of plating.

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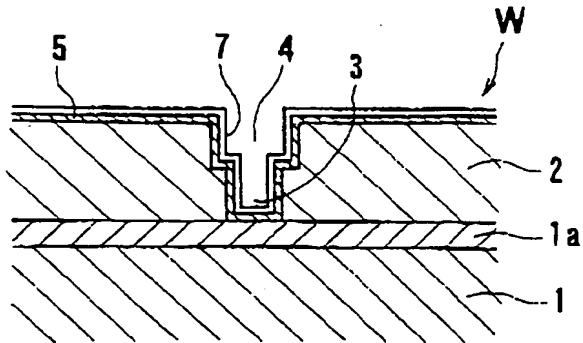
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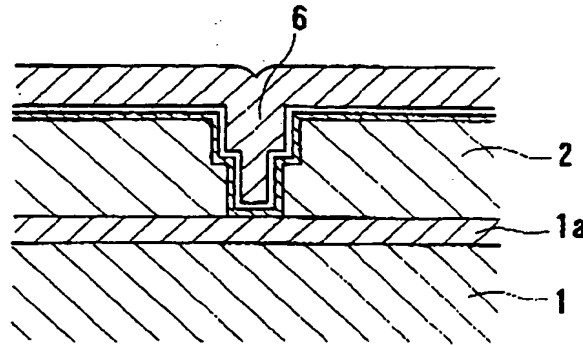
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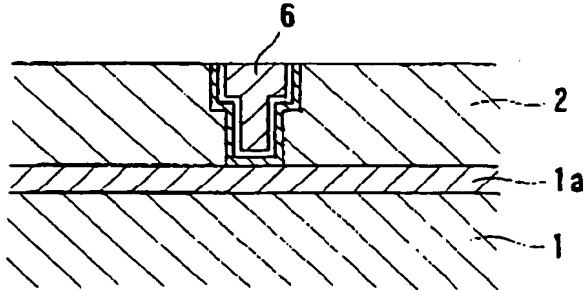
**FIG. 1A**



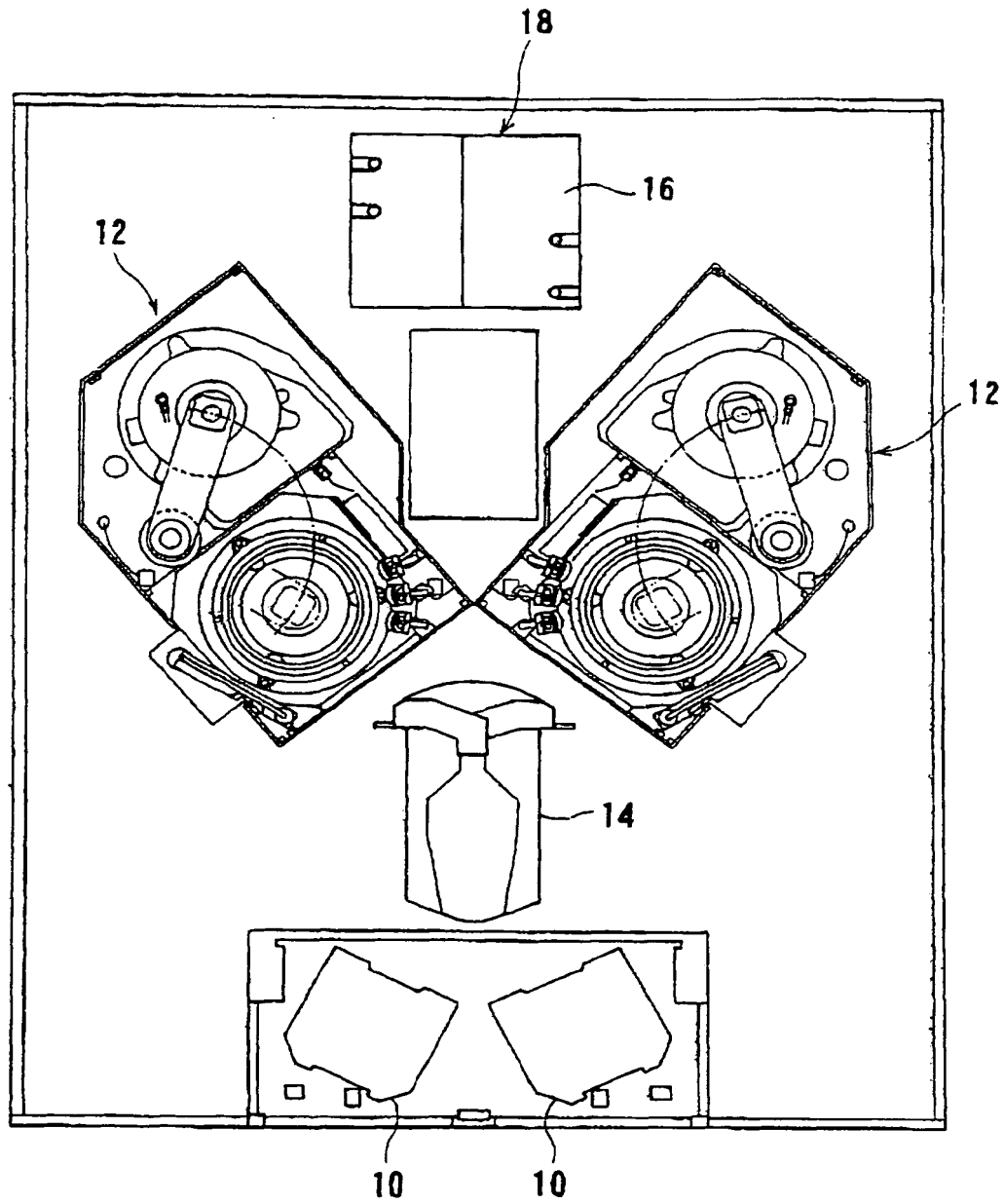
**FIG. 1B**



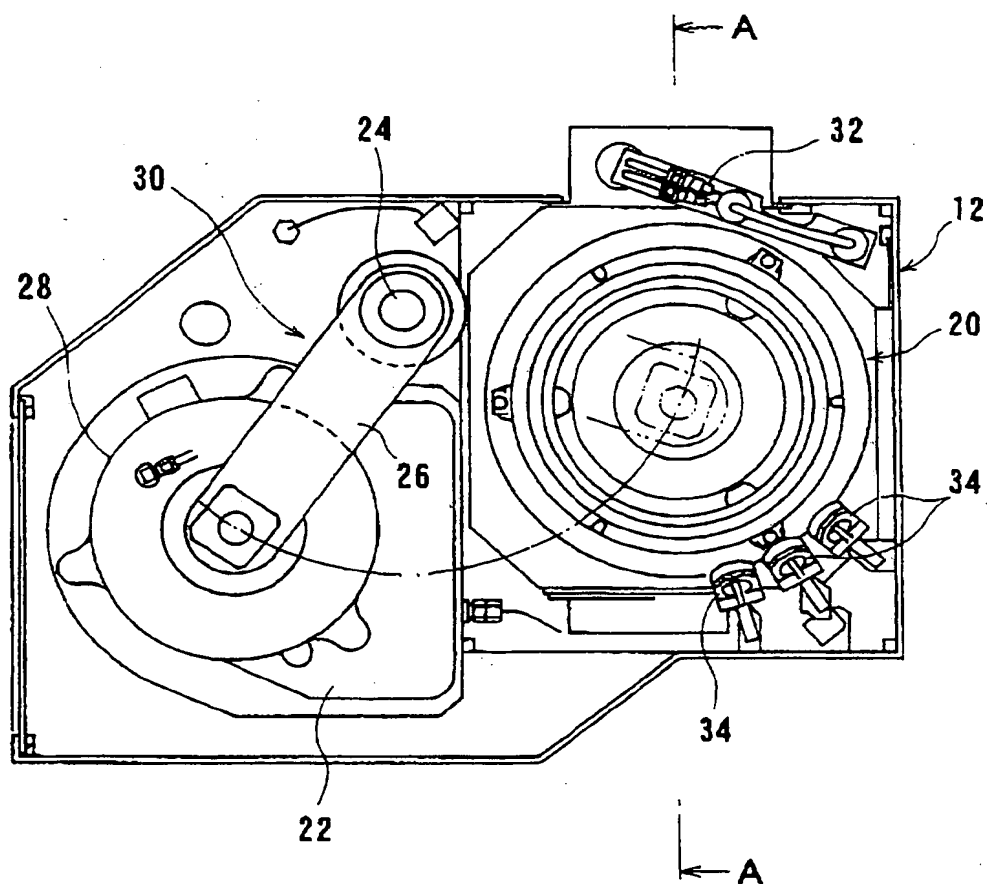
**FIG. 1C**



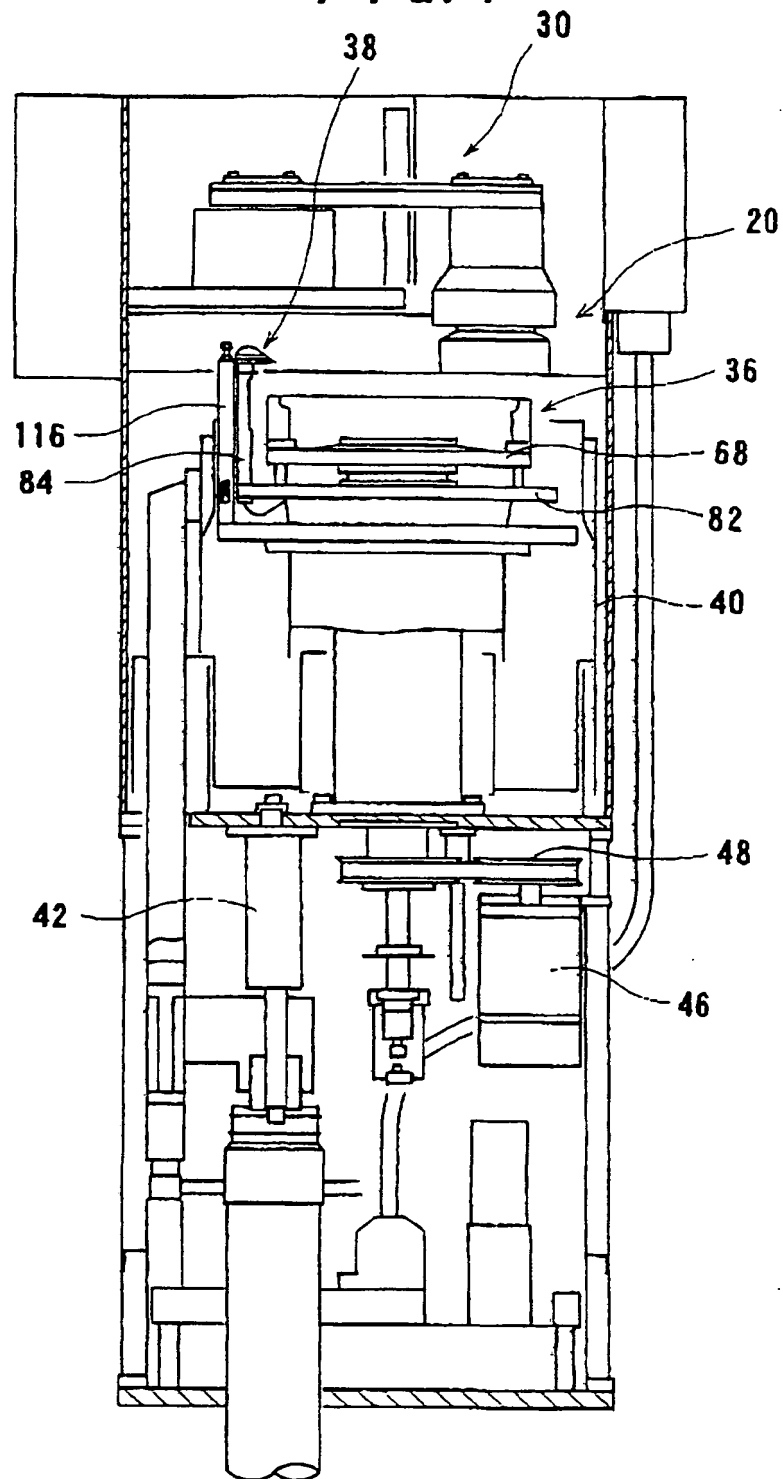
**FIG. 2**



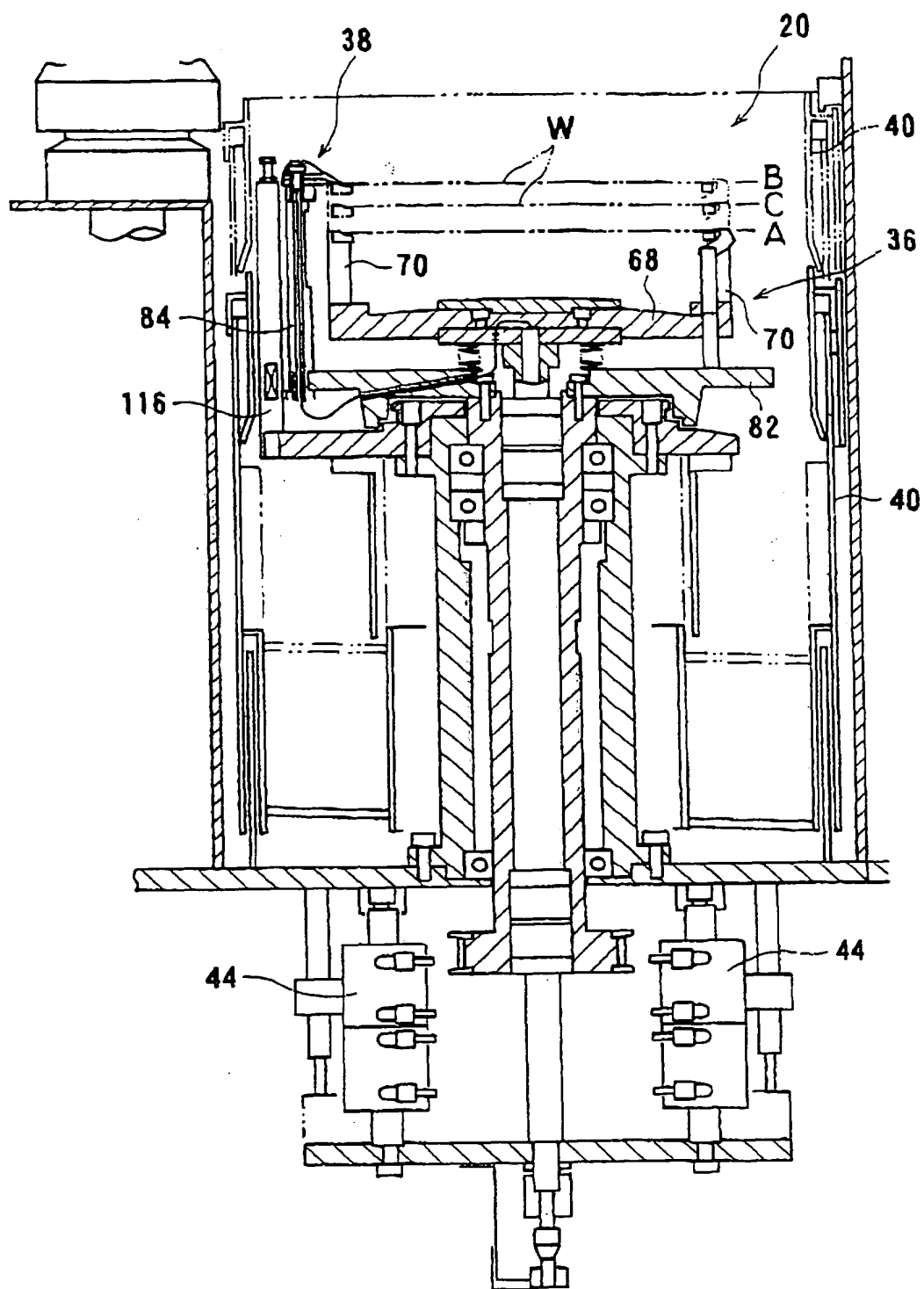
*FIG. 3*



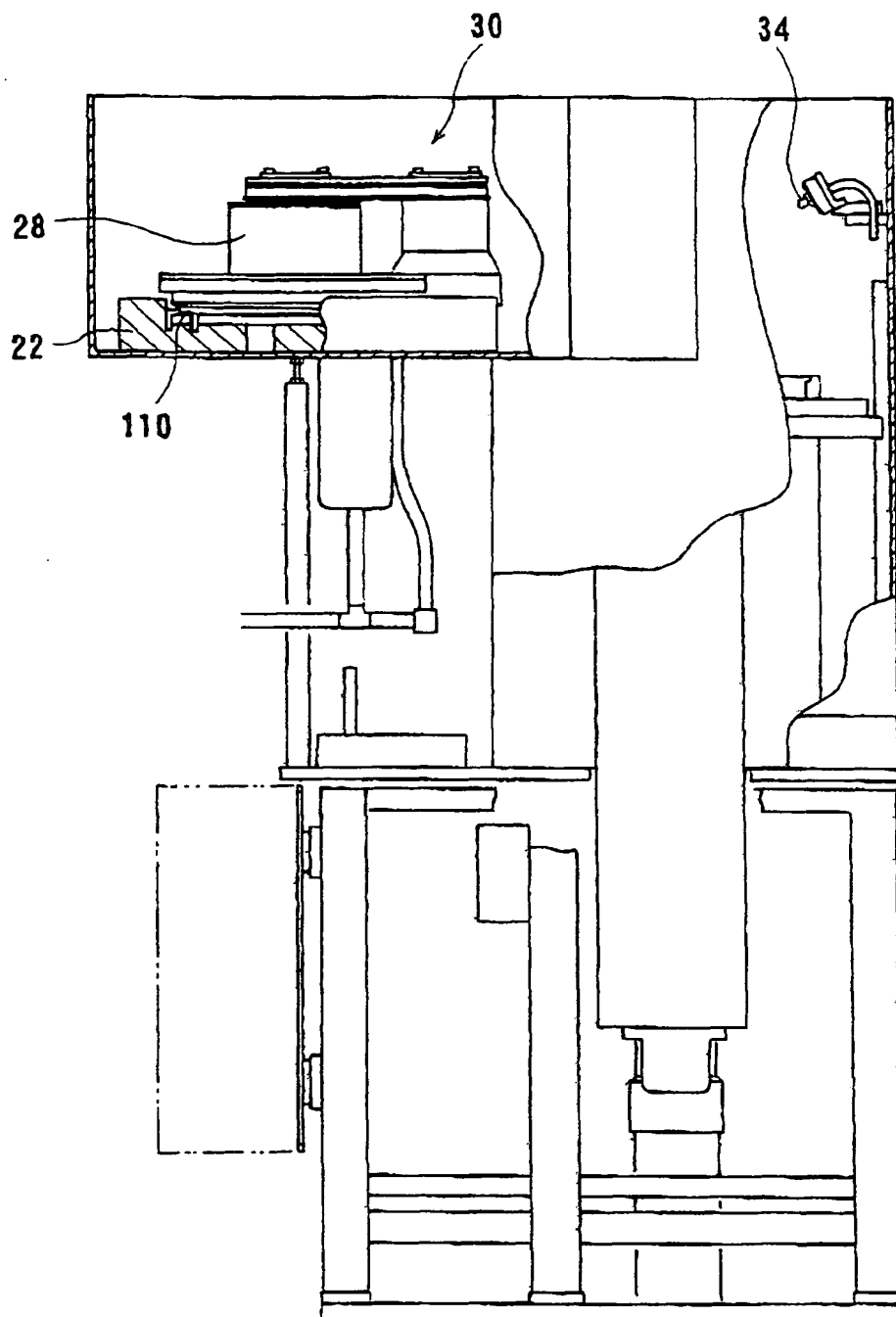
**FIG. 4**



**FIG. 5**

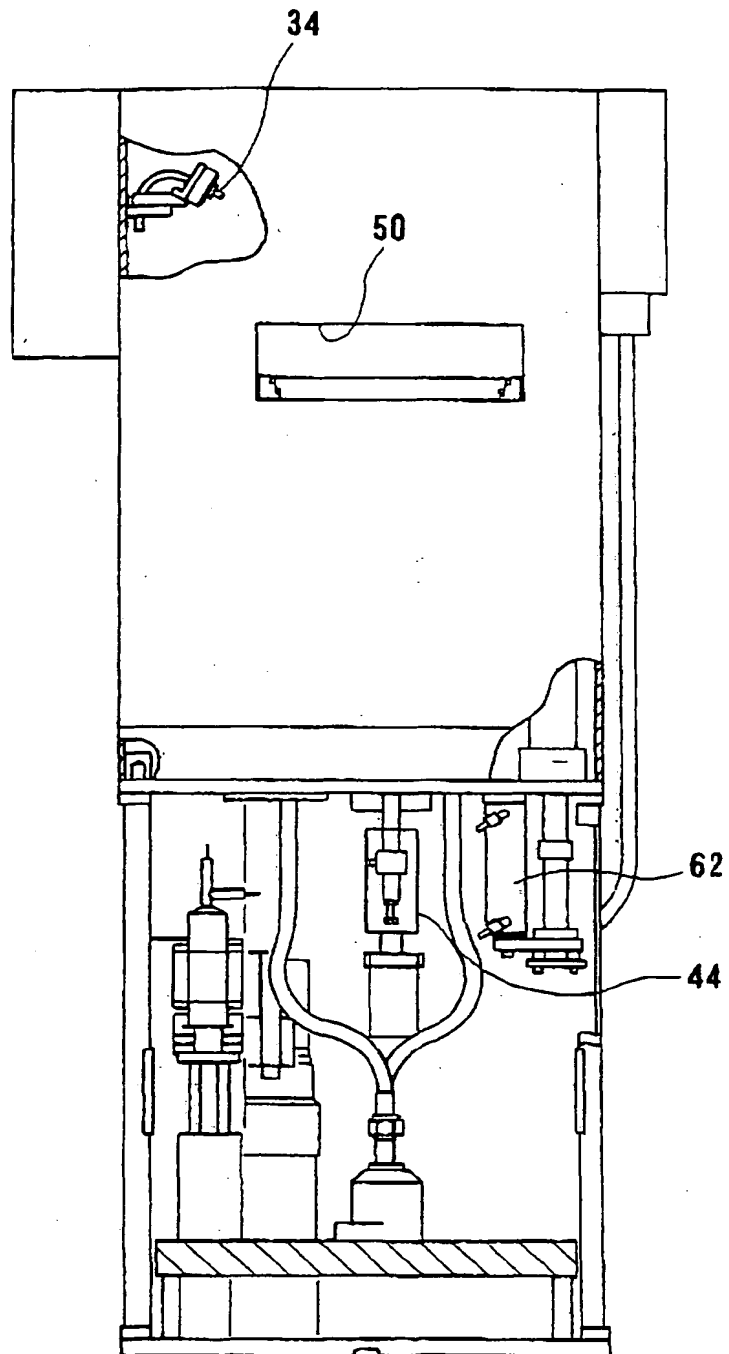


**FIG. 6**

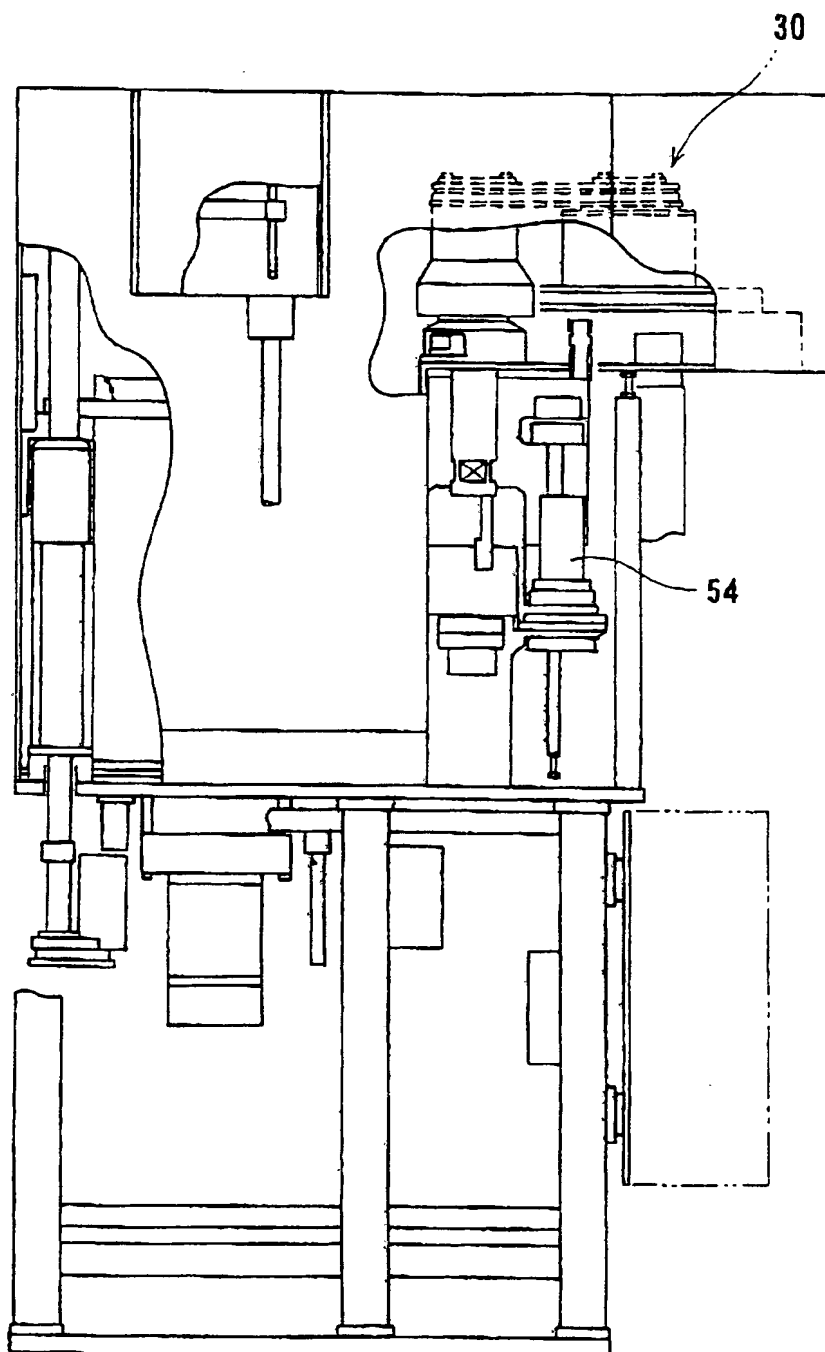




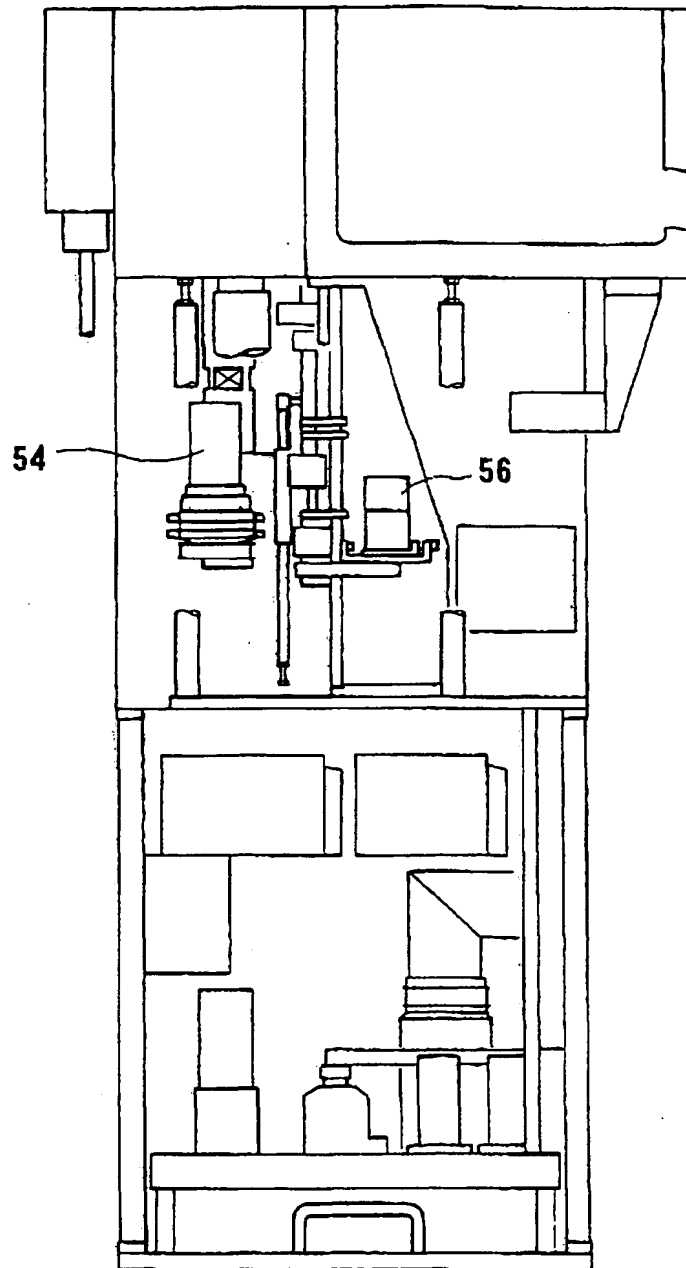
**FIG. 7**



*FIG. 8*



*FIG. 9*



*FIG. 10*

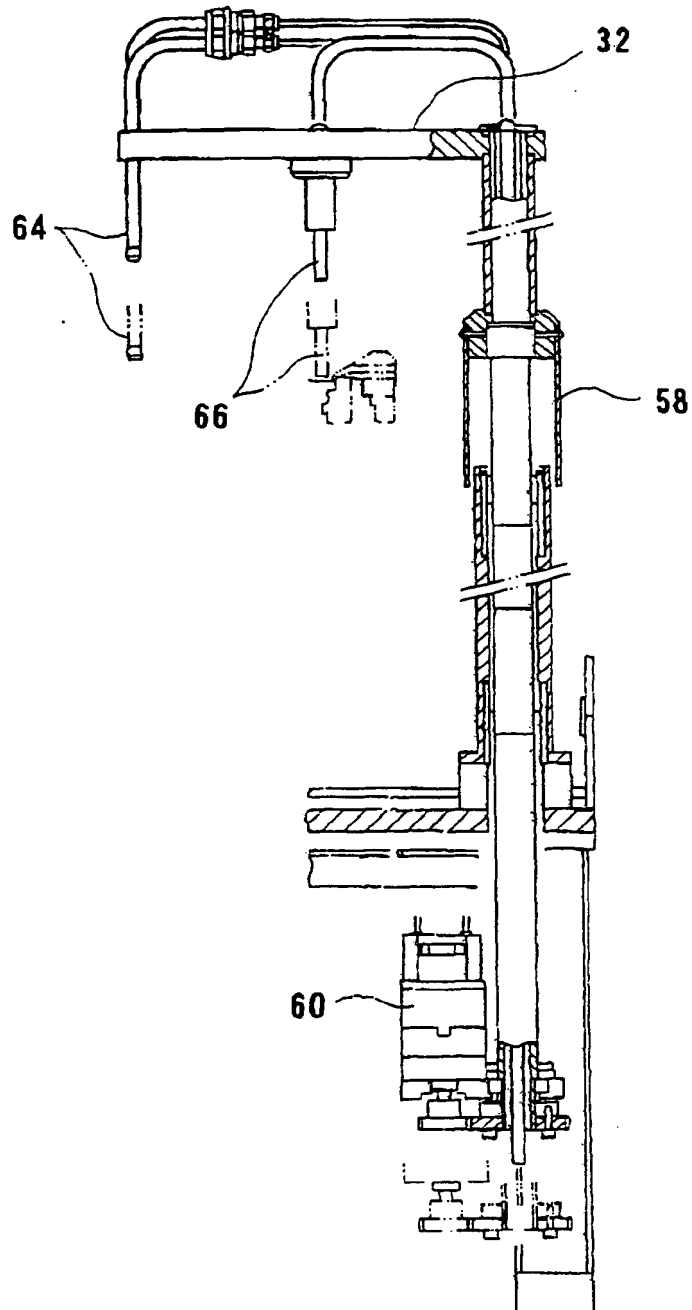


FIG. 11

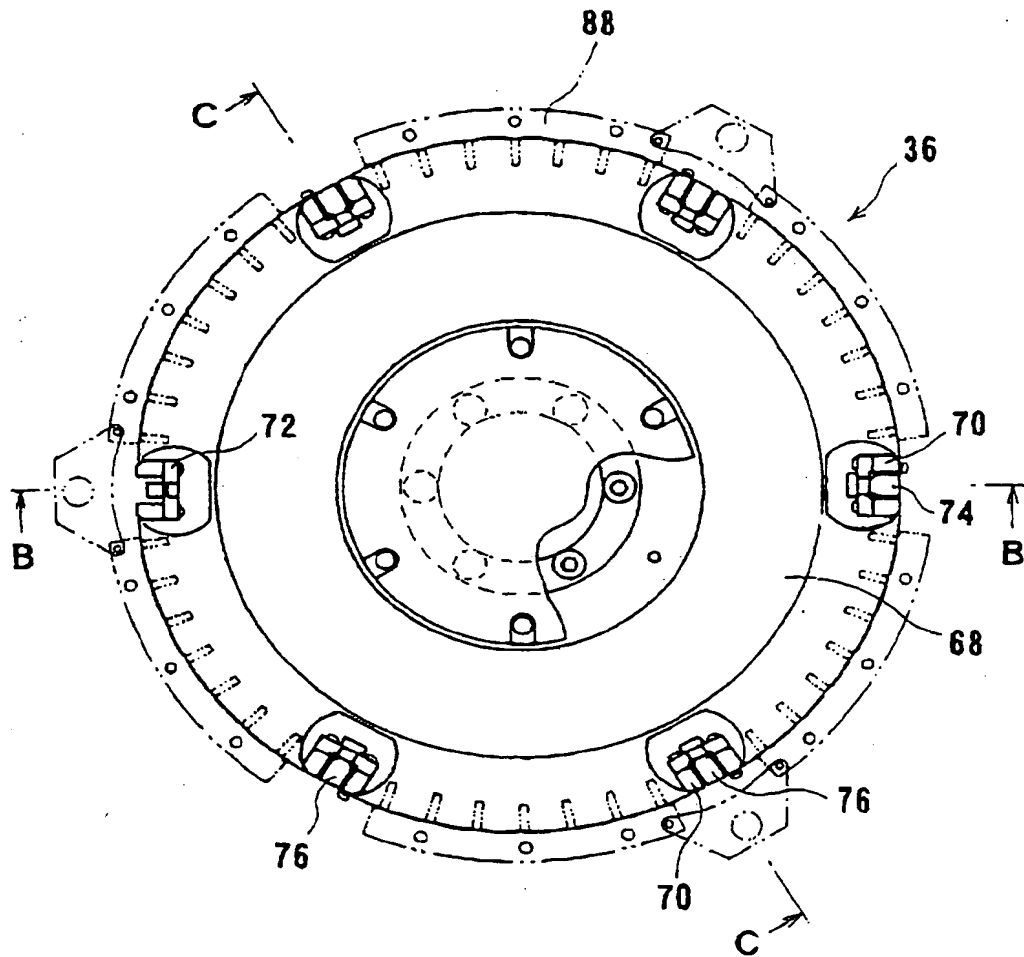


FIG. 12

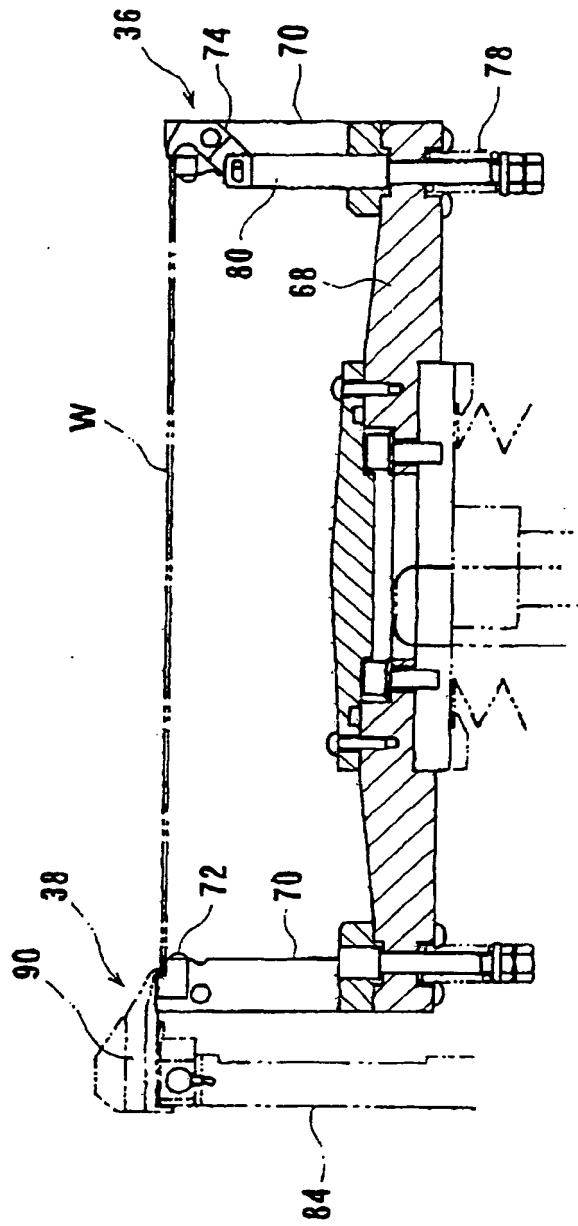
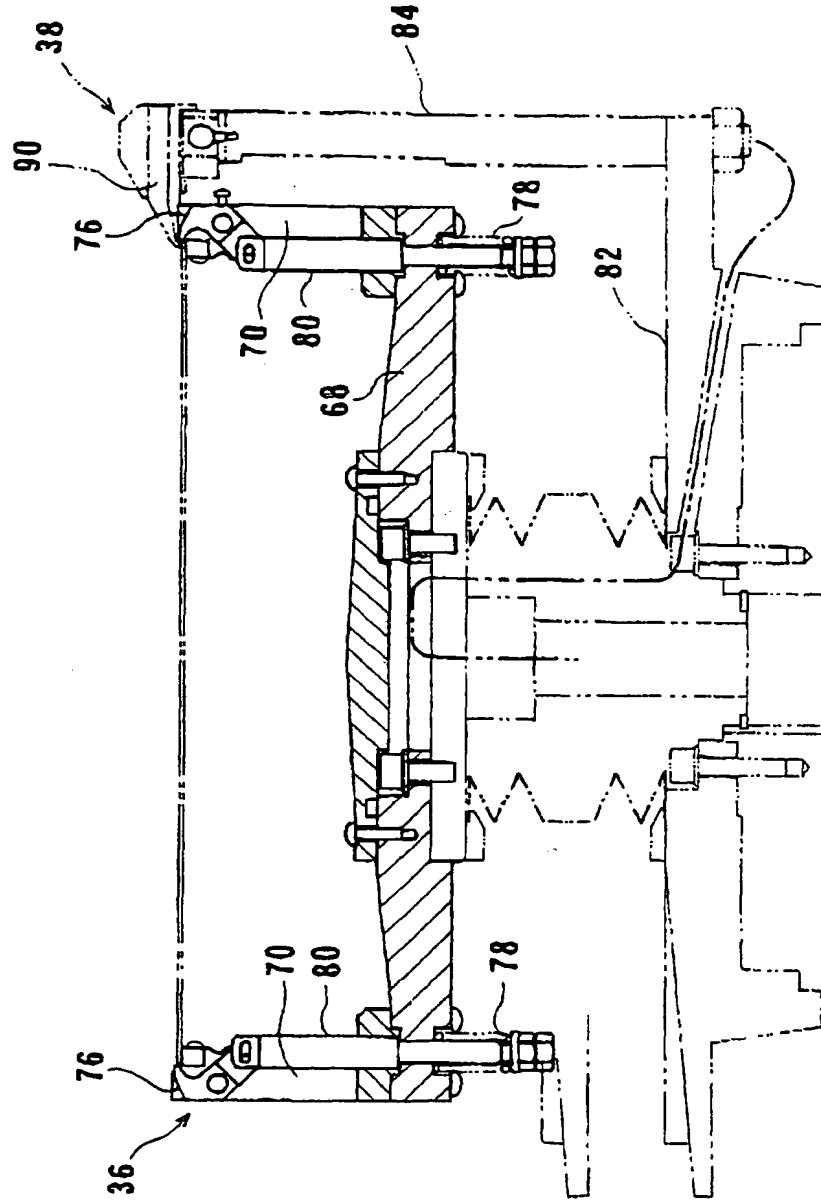
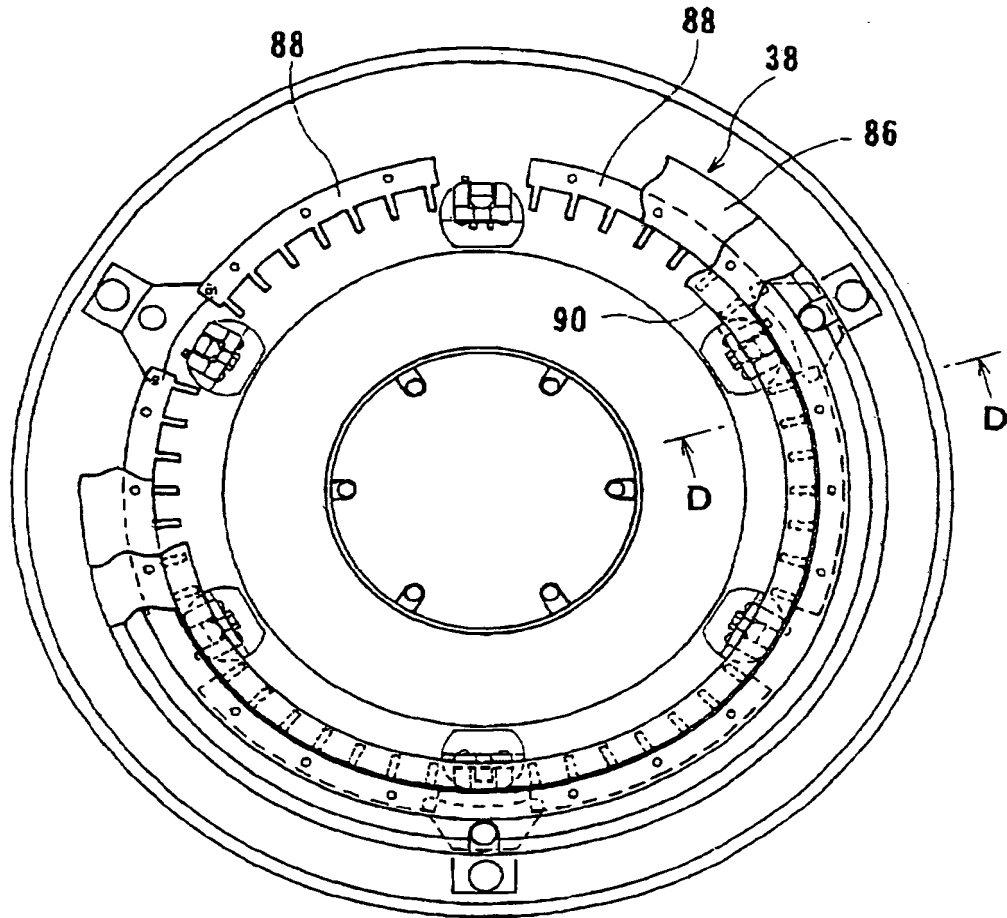


FIG. 13



**FIG. 14**



**FIG. 15**

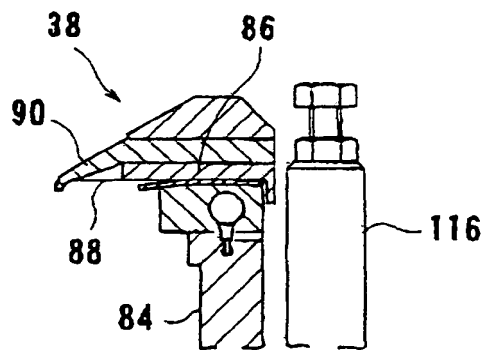




FIG. 16

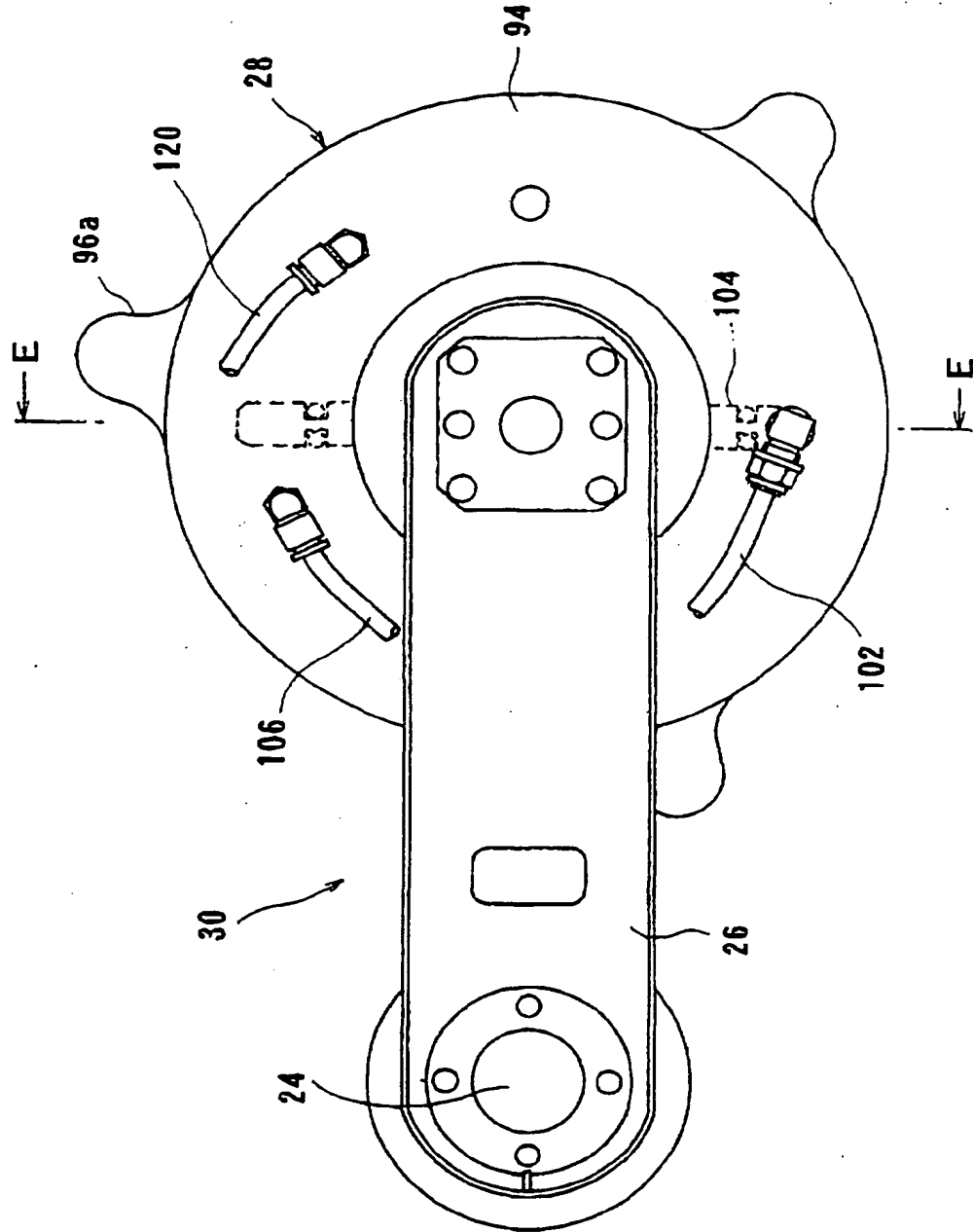
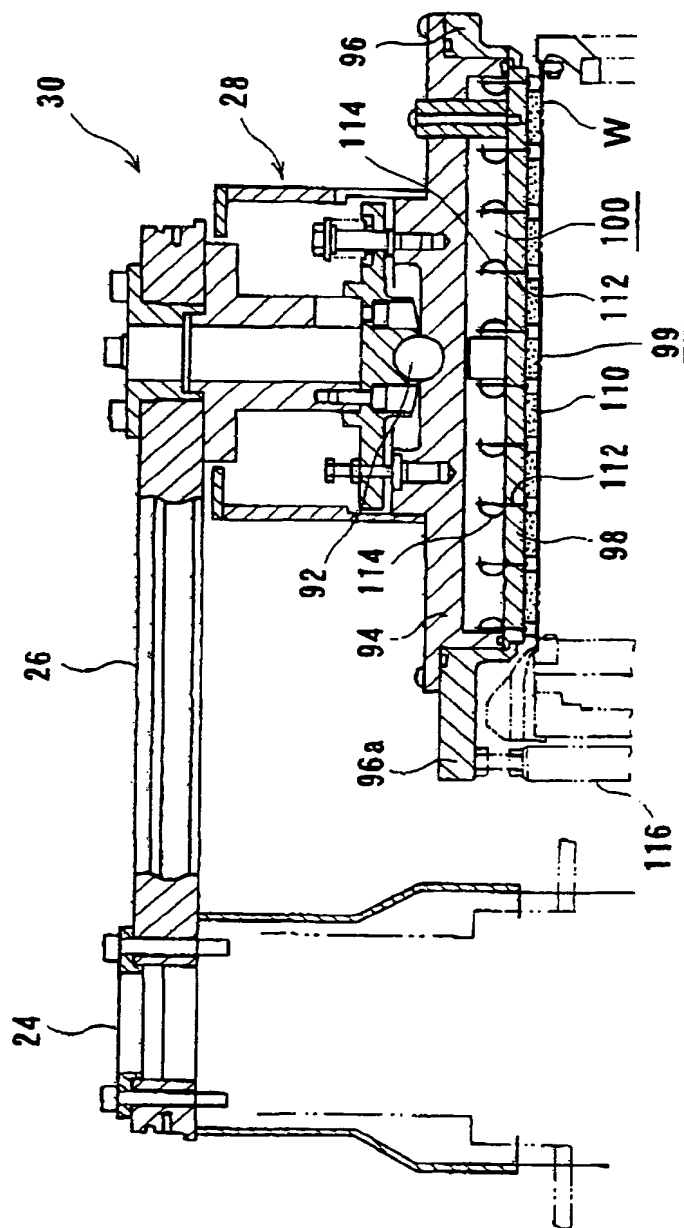
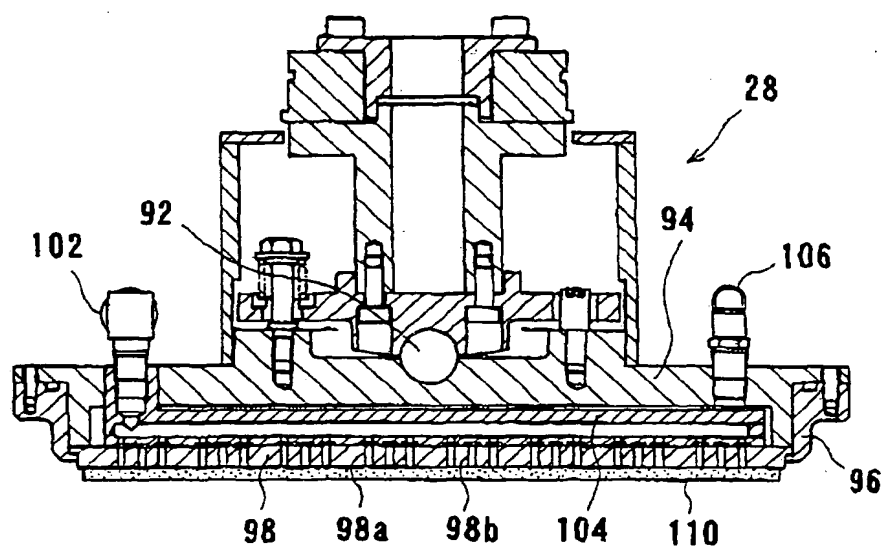


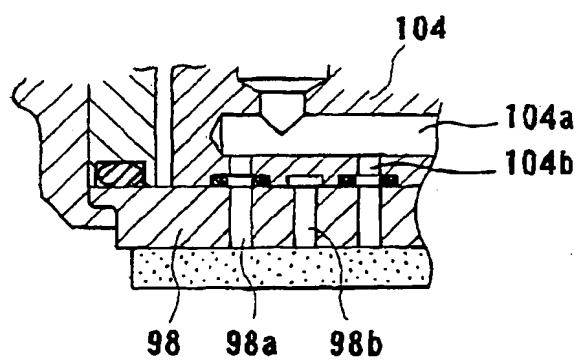
FIG. 17



**FIG. 18**



**FIG. 19**



**FIG. 20**

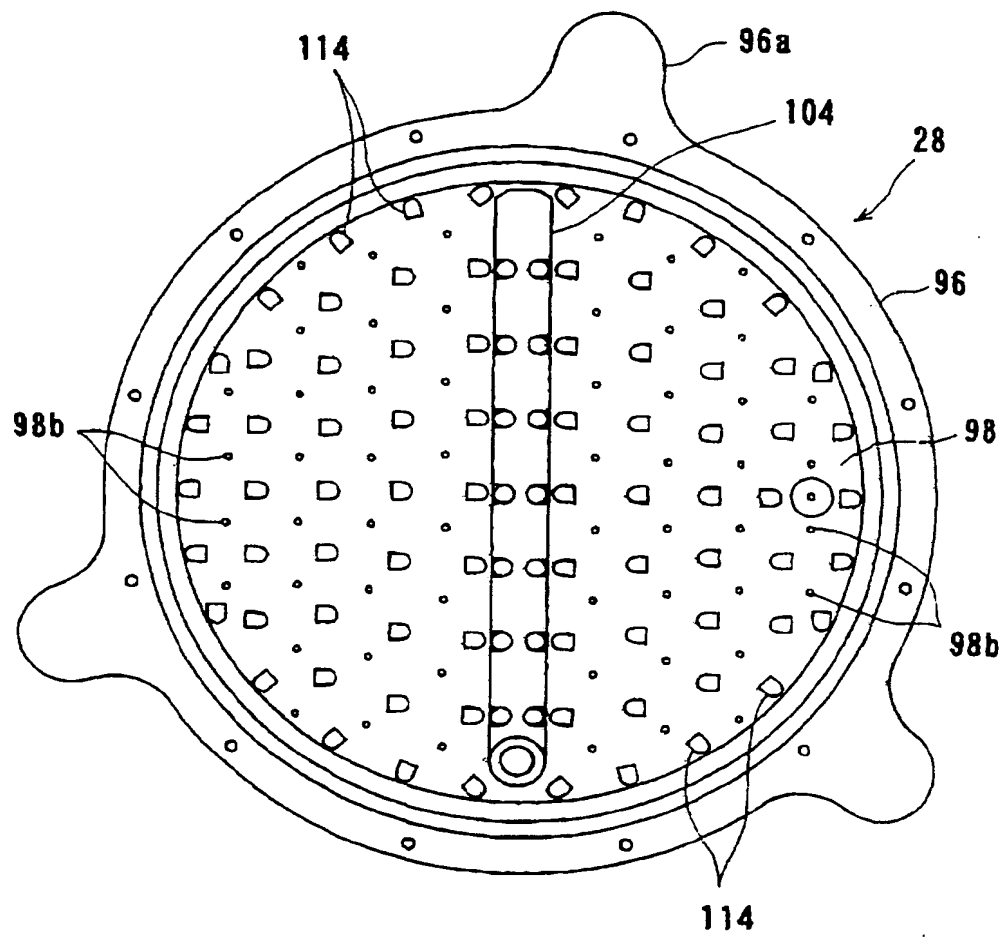
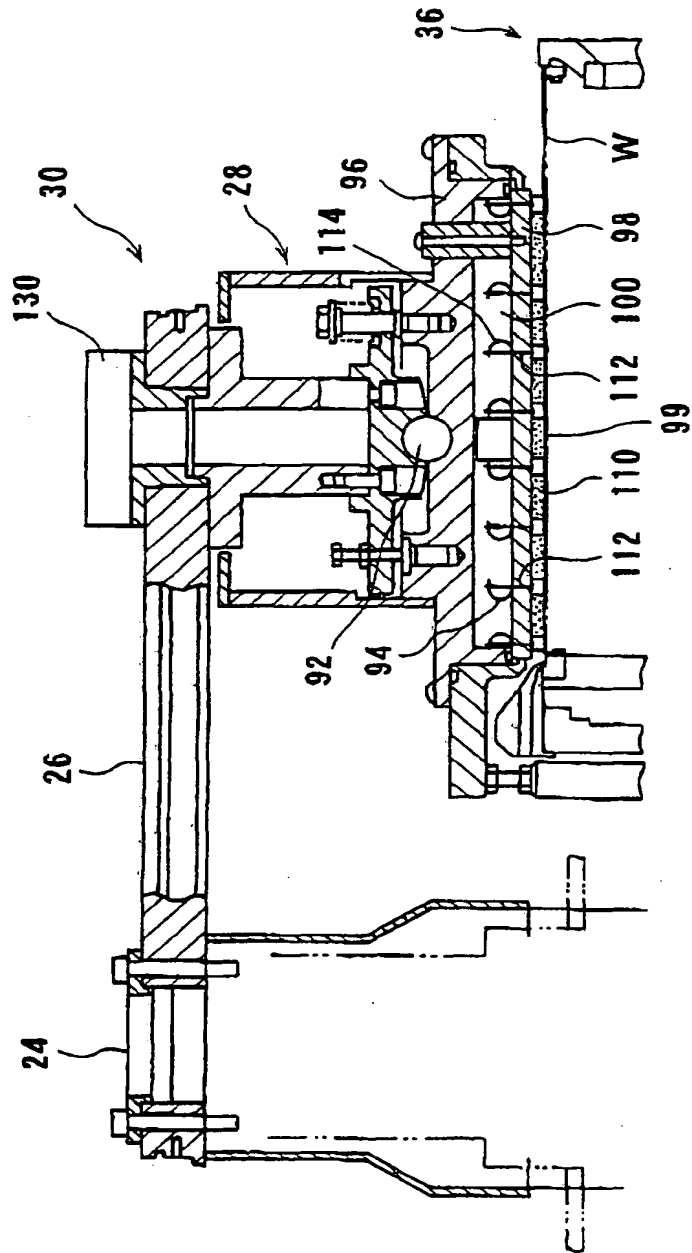


FIG. 21



*FIG. 22*

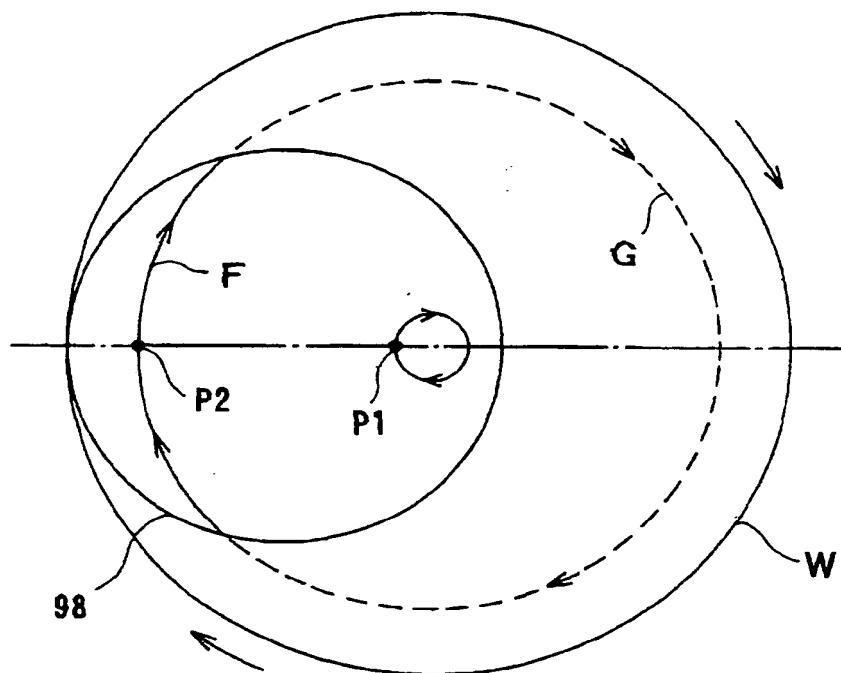
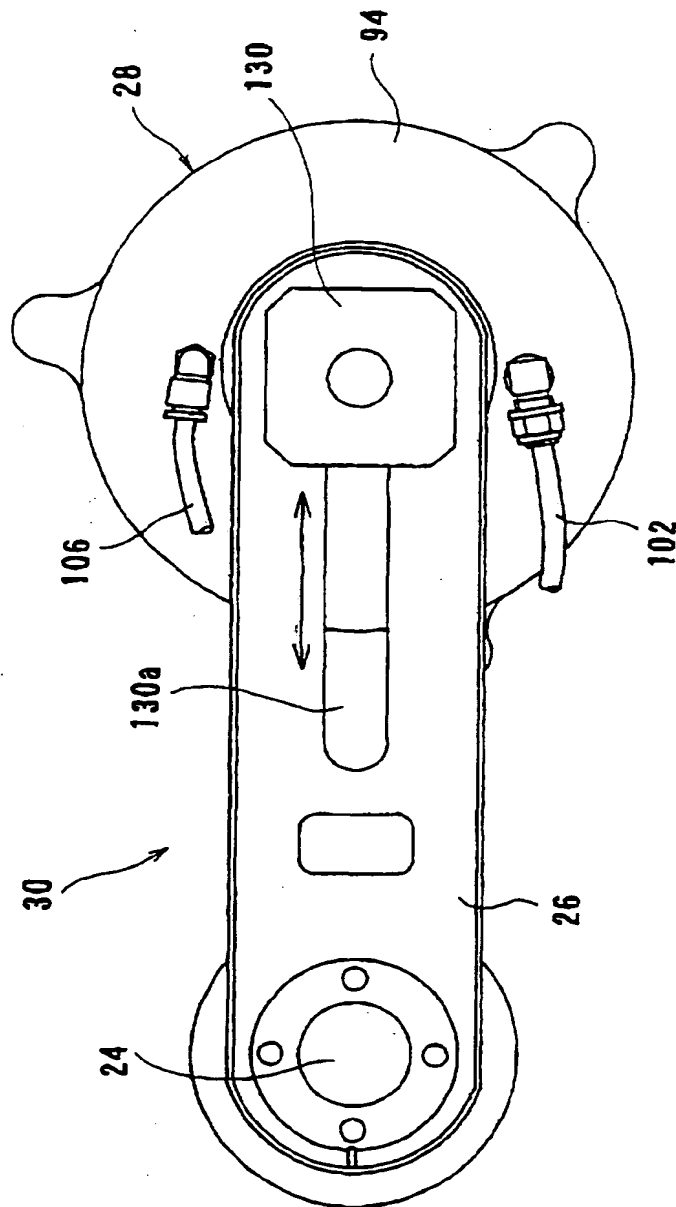


FIG. 23



*FIG. 24*

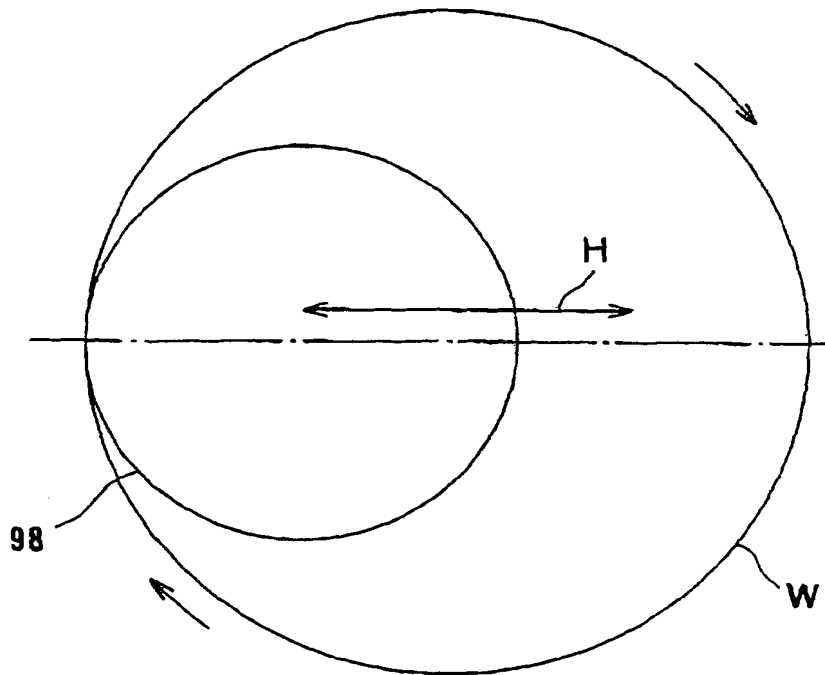




FIG. 25

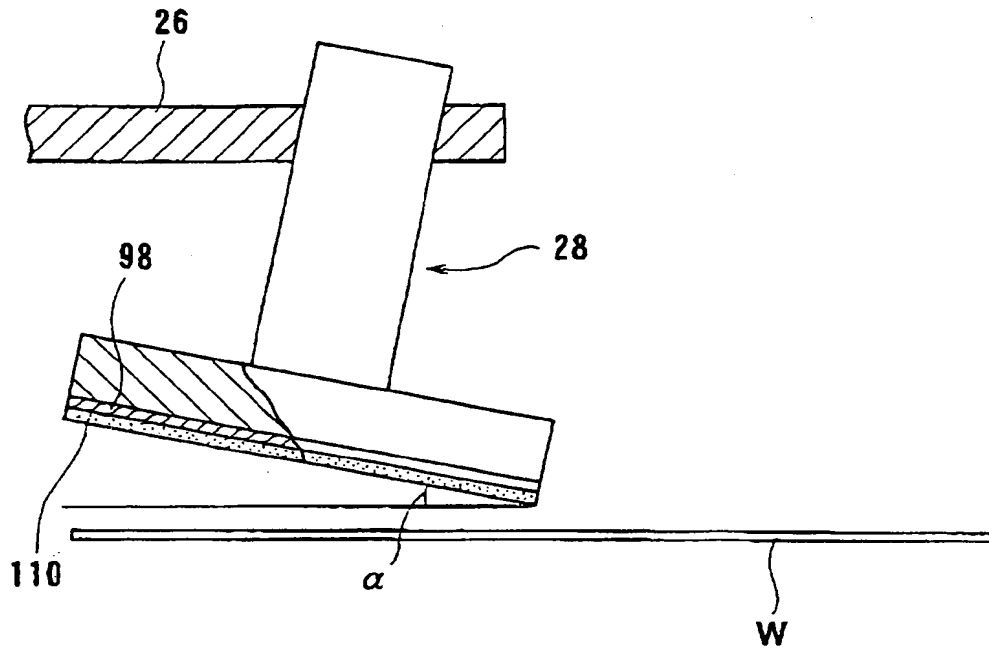
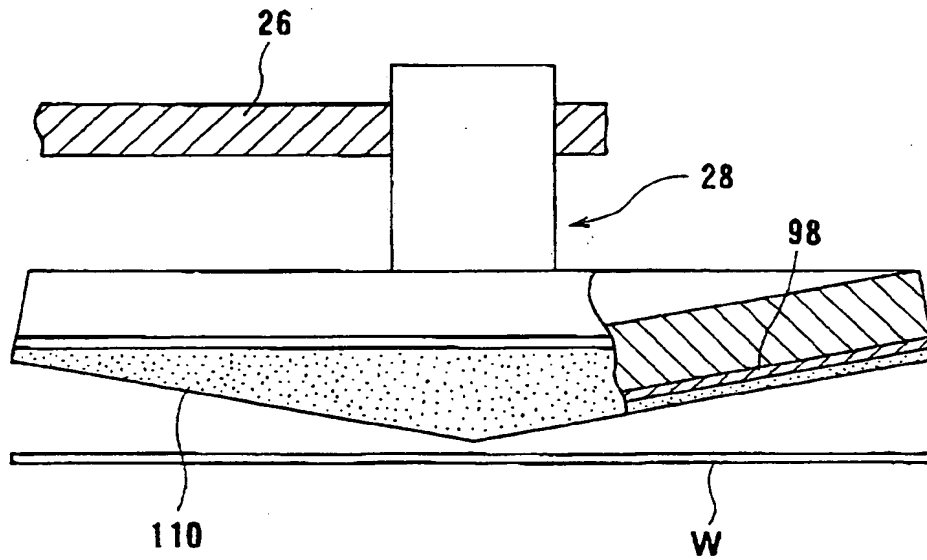
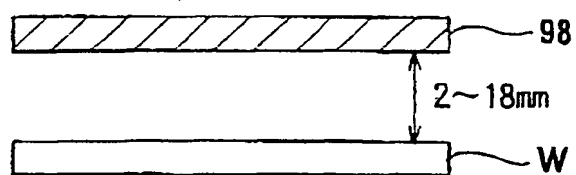


FIG. 26



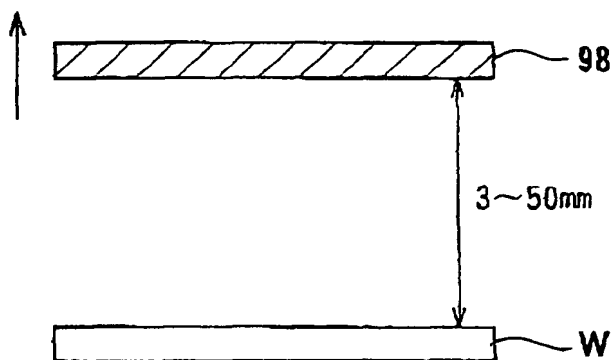
**FIG. 27A**

At the initiation of plating

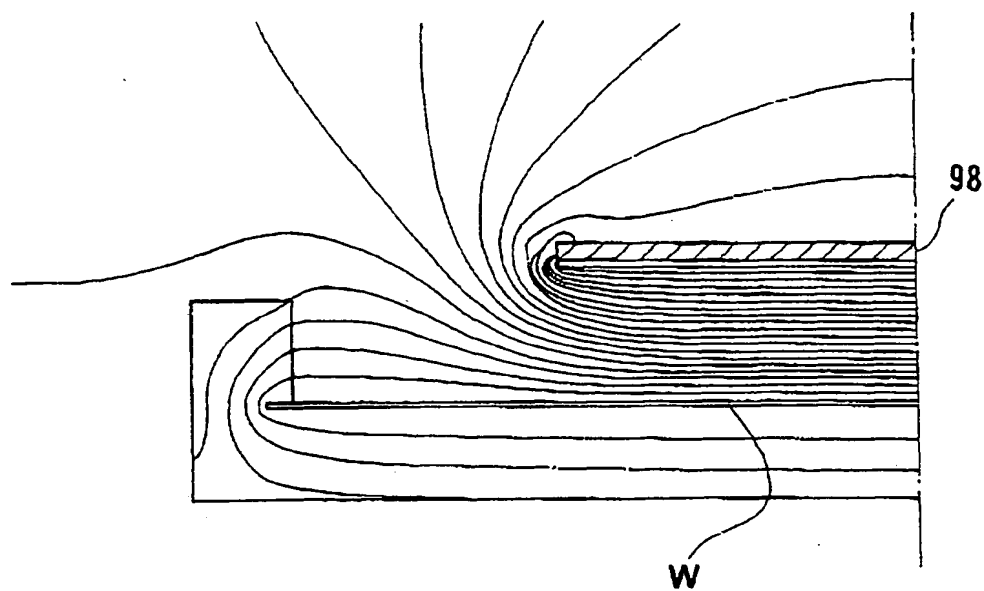


**FIG. 27B**

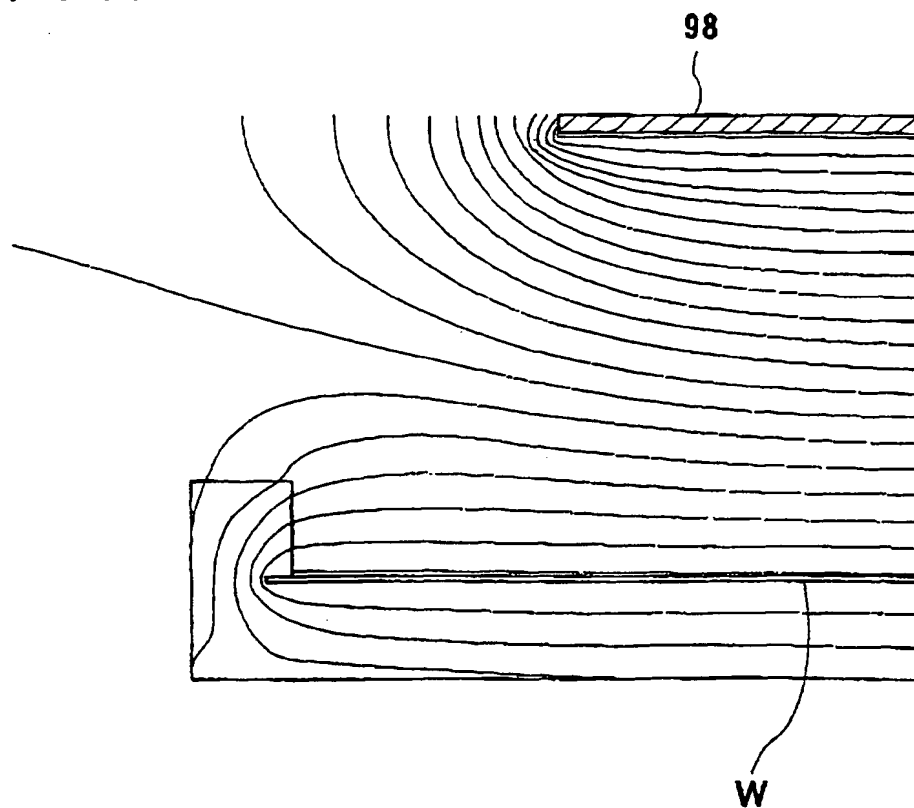
At the completion of plating



*FIG. 28A*



*FIG. 28B*



*FIG. 29*

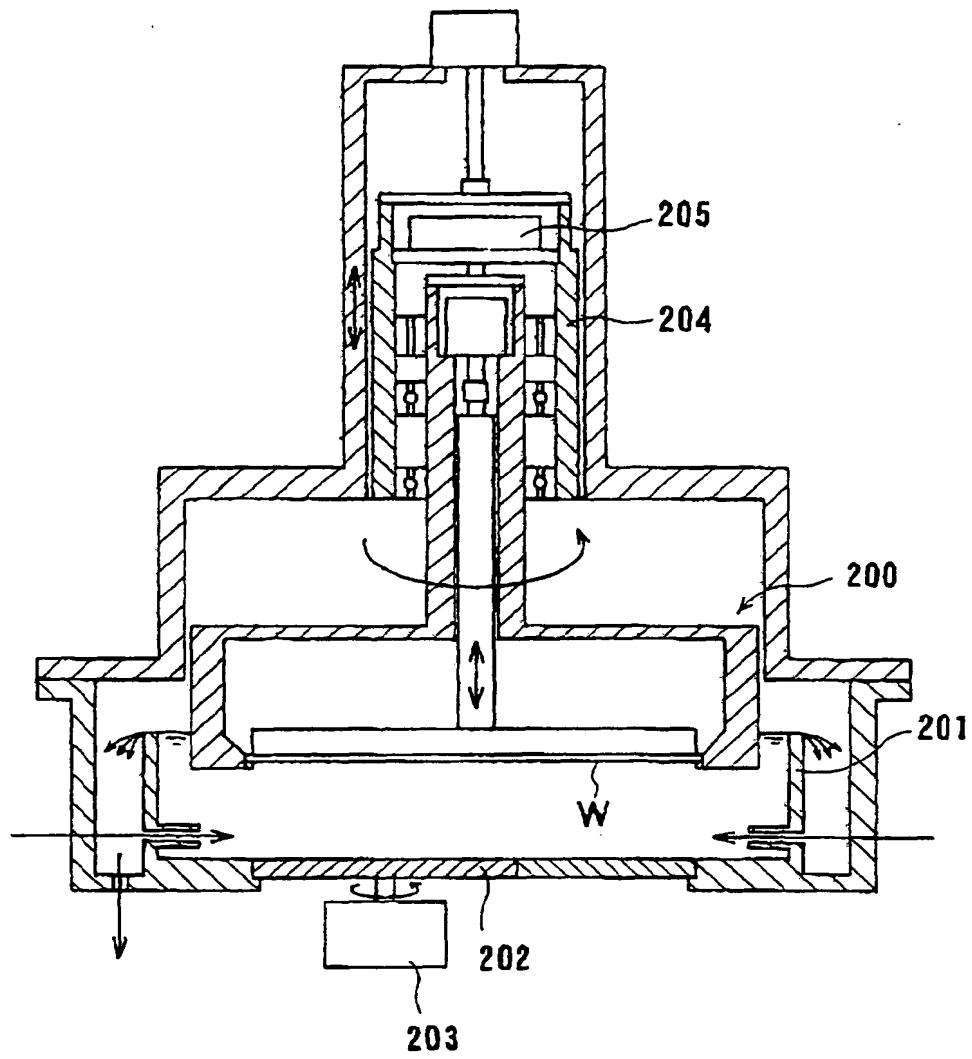
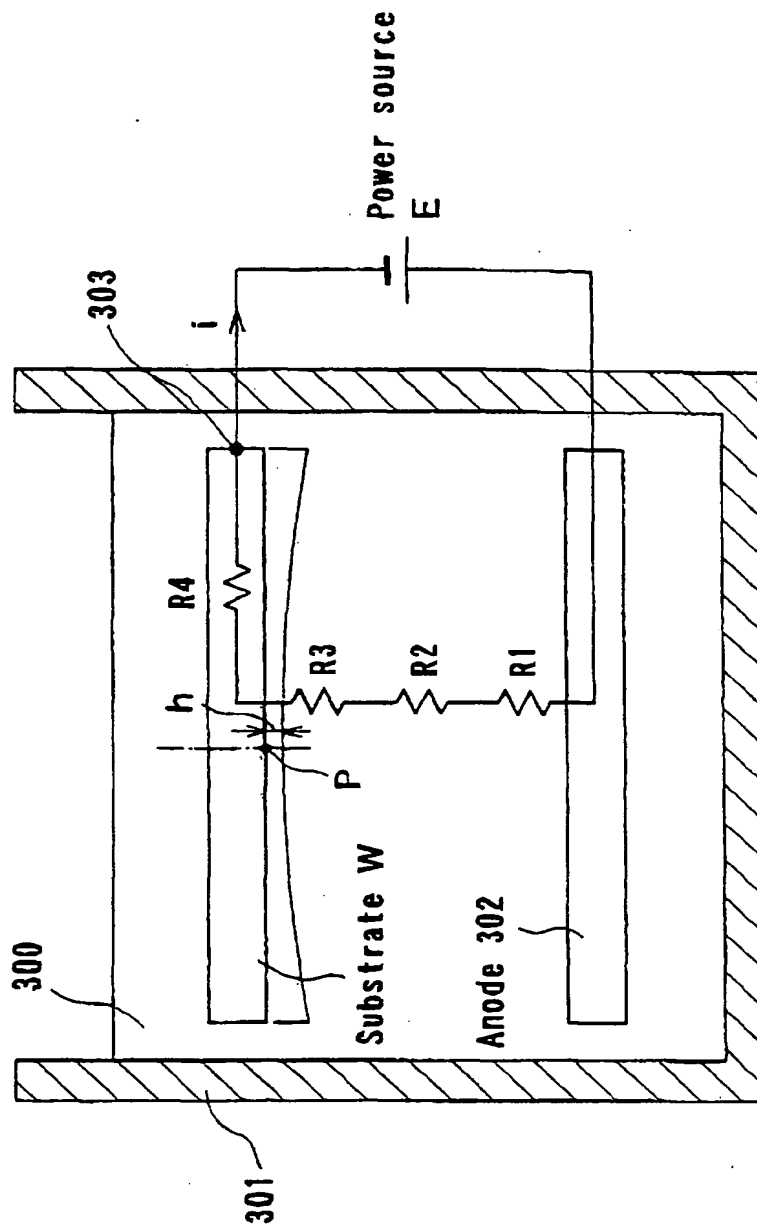
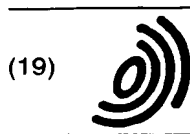


FIG. 30







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C25D 5/04

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(54) **Plating method and plating apparatus**

(57) The present invention relates to a plating method and a plating apparatus which can attain embedding of copper into fine interconnection patterns with the use of a plating liquid having high throwing power and leveling properties, and which can make the film thickness of the plated film substantially equal between the interconnection region and the non-interconnection region, thereby facilitating a later CMP processing. A plating

method comprising filling a plating liquid containing metal ions and an additive into a plating space formed between a substrate and an anode disposed closely to the substrate so as to face the substrate, and changing the concentration of the additive in the plating liquid filled into the plating space during a plating process.

EP 1 191 128 A3



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# EUROPEAN SEARCH REPORT

Application Number  
EP 01 12 1792

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 11, 30 September 1999 (1999-09-30) & JP 11 163015 A (TOSHIBA CORP), 18 June 1999 (1999-06-18) (computer translation of "detailed description" on <a href="http://www4.ipdl.jpo.go.jp">http://www4.ipdl.jpo.go.jp</a> ) * abstract *	7,11,17, 22	C25D5/08 C25D21/12 C25D5/04
X	EP 0 180 090 A (IBM) 7 May 1986 (1986-05-07) * page 4, paragraphs 2,4,5 * * page 5, paragraph 3; examples 3,4 * * figures 1,2 *	1-3,7-11	
X	PATENT ABSTRACTS OF JAPAN vol. 006, no. 257 (C-140), 16 December 1982 (1982-12-16) & JP 57 149499 A (UEMURA KOGYO KK), 16 September 1982 (1982-09-16) * abstract; figure 1 *	1-3,7-10	
X	PATENT ABSTRACTS OF JAPAN vol. 008, no. 067 (C-216), 29 March 1984 (1984-03-29) & JP 58 217700 A (TOKYO SHIBAURA DENKI KK), 17 December 1983 (1983-12-17) * abstract; figures 1-3 *	1-3,7-10	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C25D
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 248 (C-0843), 25 June 1991 (1991-06-25) & JP 03 079794 A (FUJITSU LTD), 4 April 1991 (1991-04-04) * abstract; figure 2 *	1-3,7-10	
-/--			
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 24 June 2004	Examiner Gault, N
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/02 (P04C01)





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## EUROPEAN SEARCH REPORT

Application Number  
EP 01 12 1792

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CI.7)
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 07, 29 September 2000 (2000-09-29) & JP 2000 096286 A (CANON INC), 4 April 2000 (2000-04-04) * abstract *	12, 15, 18, 21	
X	US 6 083 376 A (AKRAM SALMAN ET AL) 4 July 2000 (2000-07-04)	12-14, 18-20	
Y	* column 2, lines 42-47; claim 1; figures 1, 9 * * column 5, lines 14-28, 39-57 * * column 6, lines 7-10 * * column 7, lines 20-25 *	13	
X	US 4 430 167 A (INOUE KIYOSHI) 7 February 1984 (1984-02-07)  * column 1, lines 41-47; figures 1-3 * * column 6, lines 14-47; claim 1 *	12, 15-17, 22, 23	
X	US 4 269 672 A (INOUE KIYOSHI) 26 May 1981 (1981-05-26) * claim 1; figures 1, 4 * * column 2, lines 15-19 * * column 5, lines 28-35 *	17, 21, 23	
Y	US 3 746 633 A (ITO H ET AL) 17 July 1973 (1973-07-17) * claim 1; figures 1, 2 * * column 1, lines 59-62 * * column 2, line 70 - column 3, line 1 *	13	TECHNICAL FIELDS SEARCHED (Int.CI.7)
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 24 June 2004	Examiner Gault, N
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/82 (P4/C01)



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Application Number

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#### CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

#### LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



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Office

LACK OF UNITY OF INVENTION  
SHEET B

Application Number  
EP 01 12 1792

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-11

plating method and apparatus wherein the concentration of  
the additive is changed  
---

2. claims: 12-15, 18-21

plating method and apparatus with a moving device for moving  
the position of the substrate vis-a-vis the anode  
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3. claims: 16,22,17,23

plating method and apparatus with specific distance  
anode/substrate or with distance changing device  
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**ANNEX TO THE EUROPEAN SEARCH REPORT  
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